A
TEXT-BOOK OF HEAT

BY

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PART II

PREFACE

THIS book on the science of heat is intended to fill a place between an elementary text-book and a comprehensive treatise. It has been written to supply a want felt by many teachers and students for a work of moderate size that would represent the best that had been written on the subject by earlier well-known authorities, and at the same time include some account of recent investigations.

The work is divided into two Parts. Part I is mainly descriptive and experimental, and although the notation of the calculus is introduced and explained, the mathematical treatment has been kept as simple as possible. Part II is of a more theoretical and advanced character. It starts with the laws of thermodynamics, and after the more exact treatment of certain special subjects, including conduction, convection and radiation, passes on to an elementary consideration of statistical methods and the quantum theory. The subject of probability receives special attention.

Part I is suitable for students preparing for Higher School Certificate or Intermediate Examinations in Physics, or for a university scholarship. It is, therefore, hoped that this Part will prove of use in the higher forms of schools. The complete book has been designed to meet the requirements of those reading for a Pass Degree in Physics, and it should also furnish a good foundation for an Honours course, for which additional reading would be necessary. Books such as those mentioned on pages 837-8 would have to be consulted.

We have adopted the historical method, and have attempted to trace the development of the science from the speculations of the early philosophers on the nature of heat through the conceptions of an igneous fluid, or caloric, in the 18th century, to the dynamical theory of the 19th century, and finally to the more abstruse ideas connected with the quantum theory.

We believe that this method of treatment follows a natural order, and is important not only as possessing a cultural and educational value but also as corresponding to the logical development of the ideas and principles involved. In this we have the support of the great scientific philosopher of the 19th century, Ernst Mach, who wrote : " Let us

v

not cease to grasp the guiding hand of history. History has made all ;
history can alter all ", and we can make our own the continuation of
this quotation, " I hope this of my historical investigation, that it may
not be too tedious ".

 At the same time, modern researches relating to the subject have not
been neglected. Some recent writers have attempted to separate the
experimental from the theoretical aspects of a science—the pragmatic
from the dogmatic— but it is rather in and through the interplay between
experiment and theory that scientific progress has been most marked.
We have tried to give a clear and simple account of recent experimental
work on such subjects as calorimetry, hygrometry and low temperature
research—work which has hitherto only been accessible in technical
treatises or in the journals of the learned societies. We have also dealt
with the advances made through the development of modern statistical
methods and the quantum theory.

In Part I we have included a number of biographical notes on dis-
tinguished workers in the subject, and we have been struck by the large
part played by Scotland in the development of the science of heat. This
begins with the study of the thermometer and the laws of cooling made by
George Martine (1702-1741) of St. Andrews—work which prepared the
way for Joseph Black's discovery of specific heat. The association of
Black with James Watt is also memorable. At a later date we meet
the names of Leslie, Forbes, the brothers James and William Thomson,
Tait, Balfour Stewart, Clerk Maxwell, and many others.

The science of meteorology, which has assumed such importance in
recent years, depends, more than is often realised, upon a knowledge of
the fundamental laws of heat. We have, therefore, devoted two chapters
(XXI and XXII) to a discussion of the natural phenomena connected
with the earth's atmosphere and have attempted to describe some of the
modern developments of this branch of science.

Again, we may direct the attention of teachers to Chapter XXIII
where we have dealt fully with the vexed question of the dimensions of
thermal quantities. The distinction between macroscopic (or molar) and
microscopic thermal magnitudes is stressed ; while for the former the use
of temperature as an independent physical quantity is convenient, for
the latter this is unnecessary because of the identification of heat with
mechanical energy.

Important questions arise in connection with the accurate values of the
various physical quantities discussed and the symbols that are used to
denote them. The Tables of Physical Constants throughout the book
are in large measure based on the International Critical Tables, but we
have also found the well-known books of Kaye and Laby, and of Childs,

of great assistance, as also the comprehensive Tables of Landolt and Börnstein. The work of R. T. Birge (1929) is important in that it gives a *self-consistent* scheme of fundamental physical constants, and a revision is much to be desired in the light of the important experimental results obtained in the last decade. Some of these later determinations are given in Appendix I (p. 841).

We have adopted the symbols for thermodynamic quantities recommended by the Commission on Symbols, Units and Nomenclature to the International Union of Pure and Applied Physics, dated October 1, 1934. In the main, the symbols used in the book are in agreement with the recommendations of the Joint Committee of the Chemical Society, the Faraday Society, and the Physical Society (1937). We have, however, followed Preston in using K for thermal conductivity and k for diffusivity of temperature. The principal symbols we have employed are given on pages 526 and 847.

In accordance with the recommendation of the 1934 Commission we have stressed the importance of using the "joule" as the unit of heat measured in units of energy, and also the use of the International (Kelvin) scale of temperature. The word *joule* should rhyme with *cool*.

ACKNOWLEDGMENTS

In a work of this nature, the result of many years' teaching experience, it is not easy to acknowledge all the sources from which information has been derived. We have consulted most of the leading text-books on heat, and owe a special debt to Preston's *Theory of Heat* and to Glazebrook's *Dictionary of Applied Physics*.

We are indebted to the Air Ministry, Meteorological Office, for much assistance, and desire to acknowledge in particular the help rendered by Major A. H. R. Goldie, who has read the proofs of the chapters on meteorology and made suggestions of great value. The permission of the Controller of H.M. Stationery Office has been obtained for the reproduction of the maps from the Daily Weather Reports for the 2nd and 4th August, 1936.

The publishers have permitted the use of a large number of blocks and have been generous in the provision of many new diagrams specially drawn for this work. In this connection we are also indebted to the firm of W. and J. George, Ltd., and that of Griffin and Tatlock, Ltd. Mr. John Murray, the publisher of *The Science Masters' Book*, has given permission for the reproduction of a diagram, and the editors of that book have given help in particular sections. We have received useful information from the Cambridge Instrument Company, Ltd., and from Messrs. Kodak, Ltd.

Our thanks are due to the Universities of St. Andrews, Edinburgh,

London and Manchester, and to the various School Certificate Boards, for permission to use questions from their examination papers.

The following abbreviations are used to indicate the sources of these questions:

• C.H.S.C. -		-	Cambridge Higher School Certificate
C.U.	-	-	Cambridge University
E.U.	-	-	Edinburgh University
K.C.L.	-	-	King's College, London
L.G.S.	-	-	London General Schools
L.U.	-	-	London University
N.U.J.B. -		-	Northern Universities Joint Board
O. & C.H.S.C. -		-	Oxford and Cambridge Higher School Certificate
O.H.S.C. -		-	Oxford Higher School Certificate
St. A.U. -		-	St. Andrews University
W.B.H.S.C.		-	Welsh Board Higher School Certificate

We wish to express our indebtedness to Messrs. Macmillan and Co., Ltd., and in particular to Sir Richard Gregory for his help and courtesy throughout the time of preparation of the book, and for his ready willingness to accede to our requests. We are glad of this opportunity of making grateful acknowledgments to Dr. David Jack, who has read all the proofs, for many most valuable suggestions, and to Dr. J. C. Milligan for working through the numerical problems. We would also thank many friends and correspondents for their assistance.

It is too much to hope that the book is free from all errors or obscurities, and the authors will welcome corrections or suggestions for improvement.

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R. S. MAXWELL

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CONTENTS

PART II

A TEXT-BOOK OF HEAT

CHAPTER XXIV

THE FIRST LAW OF THERMODYNAMICS

Theories of the nature of heat. In studying the development of scientific theories we frequently find that a particular theory seems to ebb and flow, now being received, now rejected. A striking example is afforded by theories as to the nature of light, the corpuscular theory and the undulatory theory alternately gaining predominance, till at last we are forced to conclude that there is some measure of truth in each.

In heat we have two rival theories, the caloric theory and the kinetic or dynamic theory, and although the latter is generally supposed to have displaced the former, it may still be possible to restate the caloric theory in such a form as to be consistent with experimental facts. But it is doubtful whether any of the earlier exponents of the caloric theory would recognise the " substance " which they postulated in the mathematical abstraction which would nowadays take its place.

In discussing theories as to the nature of heat it is necessary to make a very important distinction and to separate the conception of heat in a material body and that of heat in free space, or as we now term it " radiant heat ". It was on account of his failure to realise this difference that much of the discussion in Leslie's treatise on Heat (1804) proved abortive. The word " heat " is now used to describe two distinct but related activities, the heat of a material body being associated with the vibrations of the particles composing it, and the radiant heat in free space being regarded as an electromagnetic disturbance travelling with the velocity of light. In each case, however, a certain amount of energy can be associated with the phenomenon, and we have now to inquire more closely into the nature of this relationship. This is, in fact, the main problem of **thermodynamics**, the branch of physics in which heat is regarded as a form of mechanical energy.

The two rival theories of heat came into conflict at the end of the eighteenth and in the earlier part of the nineteenth century. The caloric theory regarded heat as an imponderable indestructible fluid, which can pass from a hot body to a cold till temperature equilibrium is reached, while the kinetic or dynamic theory regarded heat as a form of energy, namely the kinetic energy of the ultimate particles of which the material body is composed.

In the light of our present-day knowledge we are inclined to be some-
what contemptuous of the old-fashioned "caloric theory", and to
wonder why it could possibly have survived as long as it did.   But we
must remember that this theory really did explain a large proportion of
the facts about heat which were known in the eighteenth century.*

Consider the case of two bodies at different temperatures which are
placed in contact.   It is observed that the hot body becomes colder and
the cold body hotter until finally they reach the same temperature.   This
is said to be due to "caloric" passing from the hot body to the cold
one.   Just as water at unequal heights in two vessels connected by a tube
will flow from one to the other until the levels in the two vessels are
equal, so the caloric may be regarded as flowing from the hot body to
the cold one until the temperatures are equal.   Thus in this theory
temperature may be regarded as the "level" of the caloric.   When a
piece of metal is hammered it grows hot ; this is because caloric is being
hammered out of its pores.   Similarly, when a piece of metal is bored
with a drill it becomes hot ; this is because the borings being in small
pieces cannot contain so much caloric and consequently it gets pressed
out.   So far, the observed facts fit the theory well.   There is, however,
one experimental observation which presents more difficulty.   When
a hot body is placed in contact with ice, the ice does not get warmer,
although the hot body loses caloric.   Some of the ice melts but the water
formed is at the same temperature as the ice.   We can get round the
difficulty by supposing that the caloric combines with the ice to form
water, and in so doing ceases to be *sensible*.   Thus water must be
regarded as a compound of ice and caloric.

The experiments of Rumford (1798) and Sir Humphry Davy (1799)
proved that heat could be produced by friction, but the heat thus developed
could not be traced to either of the material bodies which were rubbed
together.   These experiments brought to light facts which were in
opposition to the caloric theory, although their significance was not fully
realised at the time.   Even Carnot, over twenty years later, at first ex-
pressed his results as to the work done by a heat engine in terms of this
theory, and it was not until after the accurate experimental researches
of Joule from 1843 onwards gradually received recognition, that the caloric
theory of heat received its death-blow, and the kinetic theory triumphed.

Introduction to thermodynamics.   Thermodynamics deals with the
transformation of energy.   In the nineteenth century two important
principles were stated which were called the first and second laws of
thermodynamics.   **The first law of thermodynamics** (Joule, 1843) states
the connection between heat and mechanical work and leads up to the
great principle known as the conservation of energy.   **The second law of
thermodynamics** (foreshadowed in the work of Sadi Carnot, 1824, but re-

* See A. Wood, *Joule and the Study of Energy*, p. 30 (1925).

stated in a form consistent with the dynamical theory of heat by Clausius, 1850, and independently by W. Thomson, 1851) is concerned with the convertibility of energy, and gives us a method for determining how the amount of work obtainable from a certain quantity of heat depends on the temperatures between which the operation takes place.   It leads us to a mode of defining temperature in terms of the so-called absolute or thermodynamic scale.   Classical thermodynamics is based on these two laws and from them may be deduced a large number of relations between the physical quantities which arise in problems concerning heat.   In 1906 a new theorem was published by Nernst which is frequently termed **the third law of thermodynamics.**   This theorem may be regarded as equivalent to the statement that the absolute zero of temperature is unattainable.

STATEMENT OF THE FIRST LAW

We have already seen in Chapter XII that there is a fundamental relation between the heat (Q) taken in or given out by a body and the work (A) done by or upon that body.   This relation is symbolically expressed by the equation $A/Q = J$, where J is a constant known as Joule's Equivalent.   This equivalence between heat and work has been called the First Law of Thermodynamics which may be regarded simply as a special case of the general law of the conservation of energy.   At this stage the First Law may be stated as follows :

When mechanical energy is produced from heat a definite quantity of heat disappears for every unit of work done ; and, conversely, when heat is produced by the expenditure of mechanical energy the same definite quantity of heat is produced for every unit of work spent.

This statement is equivalent to writing the above equation in the form $Q/A = \text{constant} = 1/J$, and taking A to represent *one* unit of mechanical work.   It is sometimes convenient to use this form of equation, and employ the reciprocal of Joule's equivalent, but to avoid confusion we shall adhere to the original form of the equation.

EXPERIMENTAL VERIFICATION OF THE FIRST LAW

Measurement of Joule's equivalent. We shall now pass on to describe a long series of experiments, ranging over many years, undertaken by Joule and other workers in order to obtain an accurate value of Joule's equivalent, or, as it is frequently termed, the Mechanical Equivalent of Heat (J).

Much confusion may be caused by forgetting that J, as defined by the statement $J = A/Q$, depends on both the unit of work and the unit of heat.   The *numerical* value of J depends on the units chosen for measuring A (work) and Q (heat), but it must be emphasised that J is to be regarded as a *universal* constant (see Part I, p. 295).

Joule's early experiments. Joule's first researches * had been on electromagnetic machines, and by 1841 he had been led to consider the source of energy of his electric motor. He perceived that the consumption of zinc in the battery which drove the motor must be analogous to the consumption of coal in a furnace which would drive a steam engine. The previous year, he had communicated a paper to the Royal Society † " On the Production of Heat by Voltaic Electricity ", in which he discussed the heating effect of an electric current. He concluded from the results of his experiments " that the calorific effects of equal quantities of transmitted electricity are proportional to the resistance opposed to its passage, whatever may be the length, thickness, shape, or kind of metal which closes the circuit ". In 1843, he presented a paper ‡ to the British Association at Cork, in which he was able to derive, from the heating effect of an electric current, a numerical estimate for the " Mechanical Value of Heat ". This was the name first given to what he afterwards termed the **mechanical equivalent of heat.**

Joule expressed his result in the following terms :

" *The quantity of heat capable of increasing the temperature of a pound of water by one degree of Fahrenheit's scale is equal to, and may be converted into, a mechanical force capable of raising* 838 *lb. to the perpendicular height of one foot.*"

In a postscript to the same paper, Joule mentions that he has undertaken further experiments which prove " experimentally that heat is evolved by the passage of water through narrow tubes ". His apparatus " consisted of a piston perforated by a number of small holes, working in a cylindrical glass jar containing about 7 lb. of water ". The value thus obtained for the mechanical equivalent was 770. We can see here the germ of the idea of the celebrated " paddle wheel " experiment, because the heat obtained in this case was due to the mechanical agitation of the water.

In 1845, Joule published a paper § " On the changes of Temperature produced by the Rarefaction and Condensation of Air ". He measured the gain or loss of heat and the work done when air was compressed or allowed to expand, and obtained a mean value of 798 for the equivalent.

In the same year he described to the British Association at Cambridge the first of his paddle-wheel experiments in which the heat was evolved

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* All Joule's published papers have been collected and reissued by the Physical Society of London under the title of *The Scientific Papers of James Prescott Joule,* Vol. I, 1884, Vol. II, 1887. The descriptions of Joule's experiments given in this chapter have been largely derived from this source. An excellent account of Joule's life and work is given in *Joule and the Study of Energy,* by A. Wood.

† Joule, *Proc. Roy. Soc.,* 1840.

‡ Joule, *Phil. Mag.,* Ser. 3, Vol. XXIII, pp. 263, 347, and 435 (1843).

§ Joule, *Phil. Mag.,* Ser. 3, Vol. XXVI, p. 369, 1845.

by the churning of water in a calorimeter by a metal stirrer. The driving force was " communicated by means of weights thrown over two pulleys working in contrary directions ". The value so obtained for the equivalent was 890. As the mean for the three distinct classes of experiment he suggested a provisional value of 817.

At the British Association at Oxford in 1847, Joule gave an account of some further experiments made with the same apparatus but with greater accuracy. The mean value from tests made on the friction of water and the friction of sperm oil was 781·8.

JOULE'S PAPER OF 1849

With this short account of early work on this subject, we are now in a position to describe in detail the classic paddle-wheel experiment, in which Joule made such an accurate determination of the mechanical equivalent of heat that it was not superseded in accuracy until some twenty years later, when he himself completed a new series of experiments at the request of the British Association.

Joule's paddle-wheel experiment. In 1850, the Royal Society published a paper * in which Joule described an elaborate series of experiments which he had undertaken at Whalley Range, near Manchester, in order to make an accurate determination of the mechanical equivalent of heat. His apparatus is illustrated in Figs. 201 and 202. The method employed consisted in agitating water in a calorimeter and measuring the resulting rise in temperature.

Description of apparatus. The apparatus and the experiments will be described in Joule's own words † :

" Fig. 201 (a) represents a vertical and Fig. 201 (b) a horizontal plan of the apparatus employed for producing the friction of water,

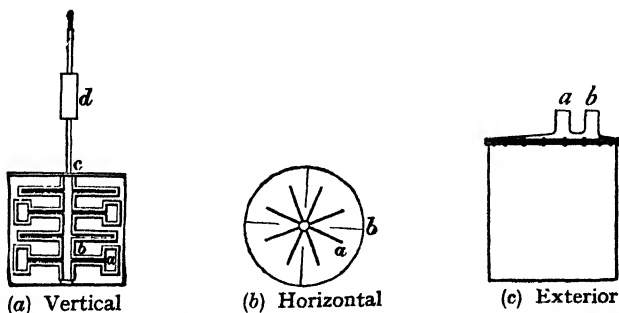(a) Vertical (b) Horizontal (c) Exterior
FIG. 201. CALORIMETER IN JOULE'S PADDLE-WHEEL APPARATUS

* Joule, *Phil. Trans.*, Vol. 140, p. 61, 1850, Part I. Read June 21, 1849.
† In the following account the numbers of the diagrams in the text have been substituted for the numbers in Joule's paper.

consisting of a brass paddle wheel furnished with eight sets of revolving arms, a, a, etc., working between four sets of stationary vanes, b, b, etc., affixed to a framework also in sheet brass.   The brass axis of the paddle wheel worked freely, but without shaking, on its bearings at c, c, and at d was divided into two parts by a piece of boxwood intervening, so as to prevent the conduction of heat in that direction.

" Fig. 201 (c) represents the copper vessel into which the revolving apparatus was firmly fitted : it had a copper lid, the flange of which, furnished with a very thin washer of leather saturated with white lead, could be screwed perfectly water-tight to the flange of the copper vessel. In the lid there were two necks, a, b, the former for the axis to revolve in without touching, the latter for the insertion of the thermometer."

" Fig. 202 is a perspective view of the machinery employed to set the frictional apparatus just described in motion. aa are wooden pulleys,
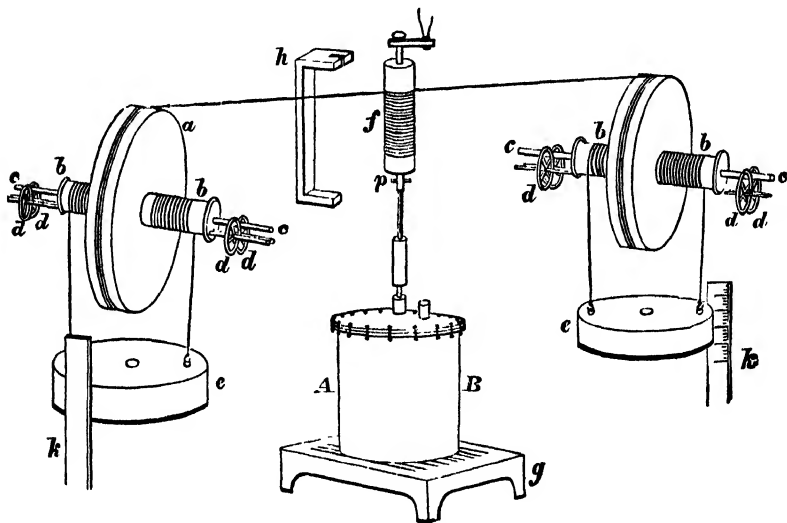

FIG. 202. JOULE'S APPARATUS, SHOWING DRIVING MECHANISM

1 foot in diameter and 2 inches thick, having wooden rollers bb, bb, 2 inches in diameter, and steel axles cc, cc, one quarter of an inch in diameter. The pulleys were turned perfectly true and equal to one another. Their axles were supported by brass friction wheels $dddd$, $dddd$, the steel axles of which worked in holes drilled into brass plates attached to a very strong wooden framework firmly fixed into the walls of the apartment.*

* " This was a spacious cellar, which had the advantage of possessing a uniformity of temperature far superior to that of any other laboratory I could have used."

" The leaden weights e, e, which in some of the ensuing experiments weighed about 29 lb., and in others about 10 lb. a piece, were suspended by string from the rollers bb, bb ; and fine twine attached to the pulleys aa connected them with the central roller f, which, by means of a pin, could with facility be attached to, or removed from, the axis of the frictional apparatus.

" The wooden stool g, upon which the frictional apparatus stood, was perforated by a number of transverse slits, so cut out that only a very few points of wood came into contact with the metal, whilst the air had free access to almost every part of it. In this way the conduction of heat to the substance of the stool was avoided.

" A large wooden screen (not represented in the figure) completely obviated the effects of radiant heat from the person of the experimenter.

" The method of experimenting was simply as follows :

" The temperature of the frictional apparatus having been ascertained and the weights wound up with the assistance of the stand h, the roller was refixed to the axis. The precise height of the weights above the ground having then been determined by means of the graduated slips of wood k, k, the roller was set at liberty and allowed to revolve until the weights reached the flagged floor of the laboratory, after accomplishing a fall of about 63 inches. The roller was then removed to the stand, the weights wound up again, and the friction renewed. After this had been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the laboratory was determined by observations made at the commencement, middle, and termination of each experiment.

" Previous to, or immediately after, each of the experiments I made trial of the effect of radiation and conduction of heat to or from the atmosphere in depressing or raising the temperature of the frictional apparatus. In these trials the position of the apparatus, the quantity of water contained by it, the time occupied, the method of observing the thermometers, the position of the experimenter, in short every thing, with the exception of the apparatus being at rest, was the same as in the experiments in which the effect of friction was observed."

Before passing on to discuss the method that Joule adopted to present his data and calculate his results, we must describe the thermometers that he used. These were three in number, and he called them A, B, and C. They were not direct reading thermometers, because on making some preliminary observations Joule " found that the number of divisions corresponding to 1° Fahr. in the thermometers A, B, and C were 12·951, 9·829, and 11·647 respectively ". These values are given to one thousandth part of a scale division, and therefore must be the mean of a

large number of readings. Joule himself, however, claimed a high degree of accuracy for his own individual readings, for he says, " since constant practice had enabled me to read off with the naked eye to $\frac{1}{20}$ of a division, it followed that $\frac{1}{200}$ of a degree Fahr. was an appreciable temperature ".

Presentation of data. Joule set out the numerical values of his experimental results with meticulous care. Concerning the first series, which comprised forty observations on the friction of water made by means of the frictional apparatus described above, he writes :

" Weight of the leaden weights along with as much of the string in connexion with them as served to increase the pressure, 203066 grains and 203086 grains. Velocity of weights in descending, 2·42 inches per second. Time occupied by each experiment, 35 minutes. Thermometer employed for ascertaining the temperature of the water, A. Thermometer for registering the temperature of the air, B."

Then follows a table giving the numerical values of the forty experiments. Table 42 is a reproduction of the first two and the last two, together with the final mean of all the experiments.

TABLE 42

No. of experiment and cause of change of temperature	Total fall of weights in inches	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3	Temperature of apparatus		Gain or loss of heat during experiment
				Commencement of experiment	Termination of experiment	
1. Friction - 1. Radiation	1256·96 0	57·968° 57·868°	2.252° − 2.040° −	55·118° 55·774°	55·774° 55·882°	0·656° gain 0·108° gain
2. Friction - 2. Radiation -	1255·16 0	58·085° 58·370°	1·875° − 1·789° −	55·882° 56·539°	56·539° 56·624°	0·657° gain 0·085° gain
39. Radiation 39. Friction -	0 1262·99	56·101° 56·182°	0·220° + 0·409° +	56·325° 56·317°	56·317° 56·865°	0·008° loss 0·548° gain
40. Friction - 40 Radiation	1262·99 0	56·108° 56·454°	0·100° + 0·036° +	55·929° 56·488°	56·488° 56·492°	0·559° gain 0·004° gain
Mean Friction	1260·248	—	0·305075°−	—	—	0·575250° gain
Mean Radiation	0	—	0·322950°−	—	—	0·012975° gain
1	2	3	4	5	6	7

Corrections. In accurate work of this nature, it is essential to make various corrections, and subsidiary experiments were made in order to determine the magnitude of these.

1. Radiation loss. This is the most important of all, and the cooling correction for the heat lost from the calorimeter has been described in Chapter VI. We see from a consideration of Table 42 that this may be nearly as much as one-sixth of the rise of temperature due to the friction, although in most cases it was not as large as that.

2. Velocity with which the leaden weights came to the ground.

3. Elasticity of the cords.

4. Friction of the pulleys.

5. Energy lost due to the vibrations of the apparatus, and principally given out as sound.

The methods of calculating these corrections are fully described in Joule's original paper and need not be dealt with further here.

Calculation of results. In order to calculate the equivalent between the heat generated and the work done in driving the frictional apparatus, it is necessary to determine these two quantities separately.

1. HEAT GENERATED. The mean rise in temperature for the forty experiments is shown in Table 42 to be $0.575250°$ F. After making careful correction for the radiation loss, Joule " gives $0.563209°$ as the true mean increase of temperature due to the friction of water ". The mass of water in the calorimeter is 93229.7 grains, and the water equivalent of the calorimeter, paddle wheel and stopper is 4240.5 grains, giving a total value of 97470.2 grains. " So that the total quantity of heat evolved was $0.563209°$ in 97470.2 grains of water, or, in other words, $1°$ Fahr. in 7.842299 lb. of water."

2. WORK DONE. This is the product of the weights driving the apparatus and the total distance through which they fell. After various corrections, the effective weight was found to be 403315 grains, and the effective height 1260.096 inches, and, after a further correction for the error due to the elasticity of the suspending string, the observations lead to a value of " 6067.114 foot-pounds as the mean corrected force ".

" Hence $\dfrac{6067.114}{7.842299} = 773.64$ foot-pounds will be the force "—or, as we should say nowadays, the work—" which, according to the above experiments on the friction of water, is equivalent to $1°$ Fahr. in a lb. of water."

Other similar experiments. In the same paper, Joule describes two similar experiments which he made. In the first, using a slightly different calorimeter, he investigated the friction of mercury, when

agitated by means of a paddle wheel. In the second, he observed the friction of cast iron, the heat being generated by means of the rotation of bevelled wheels. In both cases, the principle involved was the same as that already described in the experiments on the friction of water.

Summary of experiments. The agreement obtained for the value of the mechanical equivalent by using the several methods is quite remarkable considering the experimental difficulties involved. Table 43 records Joule's results, the fifth column being corrected for the buoyancy of the air, in view of the fact that a mass of 1 lb. weighs less in air than *in vacuo*.

TABLE 43

SUMMARY OF JOULE'S RESULTS

No. of series	Material employed		Number of experiments	Equivalent in air	Equivalent *in vacuo*	Mean
1	Water	-	40	773·640	772·692	772·692
2	Mercury	-	20	773·762	772·814	} 774·083
3	Mercury	-	30	776·303	775·352	
4	Cast iron	-	10	776·997	776·045	} 774·987
5	Cast iron	-	10	774·880	773·930	

CONCLUSIONS. Joule's conclusions on these experiments may be summed up in the closing words of his paper :

" It is highly probable that the equivalent from cast iron was somewhat increased by the abrasion of particles of the metal during friction, which could not occur without the absorption of a certain quantity of force in overcoming the attraction of cohesion. But since the quantity abraded was not considerable enough to be weighed after the experiments were completed, the error from this source cannot be of much moment. I consider that 772·692, the equivalent derived from the friction of water, is the most correct, both on account of the number of experiments tried and the great capacity of the apparatus for heat. And since, even in the friction of fluids, it was impossible entirely to avoid vibration and the production of a slight sound, it is probable that the above number is slightly in excess. I will therefore conclude by considering it as demonstrated by the experiments contained in this paper,—

1st. That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force expended. And

2nd. That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, *and taken at between* 55° *and* 60°) *by* 1° *Fahr. requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lb. through the space of one foot.*"

This value of the mechanical equivalent of heat corresponds to about 4·13 joules per calorie.

QUESTIONS •

CHAPTER XXIV   •

1. Write a short essay on the first law of thermodynamics.

2. What do you know of the early theories concerning the nature of heat? Describe some experiments which showed that the caloric theory was no longer tenable.

3. Describe some of the early experiments made by Joule from which he was able to determine the " Mechanical Value of Heat ".

4. Give an account of Joule's " Paddle Wheel " experiment, and point out clearly the corrections that he had to make to ensure a trustworthy result for the value of the mechanical equivalent of heat.

5. Describe the experiments made by Joule on the relation between the work done and the heat produced by friction when two bevelled wheels of cast iron in contact were rotated.

CHAPTER XXV

ACCURATE MEASUREMENT OF JOULE'S EQUIVALENT

AFTER the middle of the nineteenth century it became evident that there existed an exact equivalence between heat and mechanical energy, and the problem of finding an accurate value for the mechanical equivalent of heat attracted much attention from experimenters. The determinations may be divided into two classes, those in which there is a direct measurement of mechanical energy and the corresponding amount of thermal energy; and, secondly, those in which electrical energy is turned directly into thermal energy. The second type involves an accurate knowledge of the *absolute* values of the electrical units employed.

1. DIRECT DETERMINATIONS

Joule's " friction balance " experiments. In 1878, Joule completed a further series of experiments * on the mechanical equivalent of heat, which he had undertaken at the request of the British Association. His apparatus has been described as " a kind of friction balance " designed by Hirn.

The method adopted for heating the water in the calorimeter was, as before, by means of a rotating paddle, but in the new apparatus the calorimeter was suspended by a bearing on the vertical axle of the paddle. When the paddle was set in rotation, the calorimeter tended to rotate in the same sense. This rotation was, however, prevented by means of an applied couple produced by the action of a fine silk cord passed round a groove in the surface of the cylinder and acted on at its ends by known forces. The work done could be measured from a determination of the moment of this couple and the number of revolutions made.

DESCRIPTION OF JOULE'S APPARATUS. The apparatus is illustrated in Fig. 203. " A massive wooden framework, *aa*, resting on the asphalted floor of a cellar, is still further strengthened by means of timber abutting against the walls on every side. The perpendicular shaft *b* is supported by a conical collar turned on it at *c*. It is revolved, along with the fly-wheel *f*, weighing about 1 cwt., by means of the doubling hand-wheels

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* Joule, *Phil. Trans.*, 1878, Part II.

de. A counter is placed at *g*, for the purpose of reading off the number of revolutions. The calorimeter *h* has an accurately turned groove, from which silk threads pass over the light, accurately turned pulleys *jj*, to the scales *kk*. . . . Three sides of the frame are boxed in permanently ; the fourth, or front, has shutters with windows which can be removed at pleasure. A delicate thermometer, suspended within the frame, is
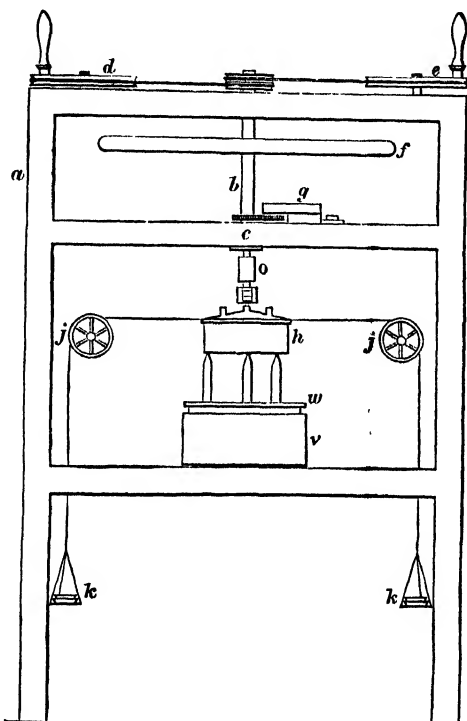

FIG. 203. JOULE'S " FRICTION BALANCE " APPARATUS

observed through a telescope, as is also the thermometer employed in reading the temperature of the calorimeter.

" Fig. 204 represents the section of the calorimeter, with its paddle, all of stout sheet brass ; and Fig. 205 gives a plan of the same. The dotted lines in the latter show the position of the fans in the upper part. The axle of the paddle works easily in the collar *m*, and is screwed into the boxwood piece *n*." " It will be seen in Figs. 204 and 205 that there are four stationary vanes in the calorimeter, and two sets of rotating vanes, each of five arms, the upper set being fixed on the axis 9° behind the lower set. Hence no two vanes pass the fixed ones at the same moment ; and inasmuch as the momentary alteration of resistance at

crossing takes place 40 times in each revolution, the resistance may be considered as practically uniform."

METHOD OF EXPERIMENTING. " In making an experiment for the equivalent, the weight of the calorimeter filled with distilled water was first
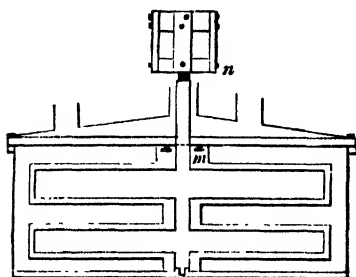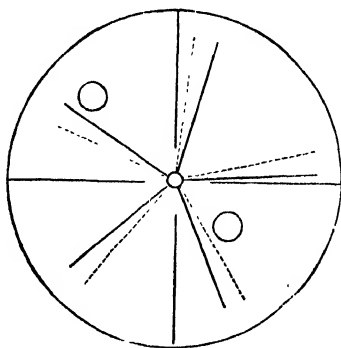

FIG. 204. SECTION OF CALORIMETER

FIG. 205. PLAN OF CALORIMETER

carefully ascertained. It was then screwed on to the axis, and the fine silk cords attached to the scales, kk, Fig. 203, were adjusted. Thermometer A was then introduced into one of the tubulures, and after sufficient agitation of the water by means of the paddle itself, its indication was observed through a telescope. The thermometer was then removed and a caoutchouc stopper placed in the tubulure. The axle was then brought rapidly up to the velocity which produced friction sufficient to raise the weights about a foot from the ground. My son, Mr. B. A. Joule, who turned the wheel, could, by observing the position of the scales in a mirror, keep them very steadily at a constant height during the whole time of revolution. The wheel having been rapidly brought to a standstill, the temperature of the calorimeter was again ascertained.

" In the experiments . . . the number of revolutions of the axis when the weights were off the ground was added to half the number occupied in the acts of starting from rest and returning to rest.

" Previously to, and subsequently to, every such experiment others were made under similar conditions as to the observation of temperatures, etc., in order to ascertain the effect of the atmosphere on the temperature of the calorimeter." Thus the radiation correction was made as before.

In the later stages of the investigation a special " hydraulic supporter " was fitted below the calorimeter so as to reduce the pressure on the bearing and the consequent metallic friction.

CALCULATION OF RESULTS. As in the case of Joule's earlier experiments, it was necessary to measure the heat generated and the work done in order to calculate the mechanical equivalent of heat.

1. Heat generated.   The water equivalent of the calorimeter and its fittings was measured by a method described in the paper.   This when added to the mass of water in the calorimeter, and multiplied by the observed rise in temperature, gives the quantity of heat absorbed.

2. Work done.   Let r = the radius of the calorimeter, and w = the sum of the suspended weights.   Then $wr = G$, the moment of the couple tending to turn the vessel.   Thus the work done in turning through an angle θ is $G\theta = wr\theta$, and the work done in turning through n revolutions is $2\pi nwr$.

The mean value deduced by Joule from some 34 experiments at a temperature of 60° F. was $J = 773 \cdot 369$ foot-pounds per thermal unit in a latitude of 53° 28½′ N. at Manchester.

If this is corrected to the latitude of Greenwich, and for water weighed *in vacuo*, the equivalent is finally reduced to $772 \cdot 55$ foot-pounds per B.Th.U.

Rowland's experiments.   In 1879, Rowland carried out an elaborate series of experiments on the mechanical equivalent of heat, at Baltimore. He used a friction-balance method almost identical with that of Joule, which has already been described.   A rise in temperature of the water in a calorimeter was produced by churning with a rotating paddle wheel, and the couple needed to keep the calorimeter from turning was measured. Rowland's experiments show an improvement in accuracy over Joule's researches in three ways :

(1) He obtained a larger rise in temperature in a short time.   This involved a larger number of vanes and the employment of greater power for rotating the paddle wheel.   In Rowland's apparatus this was driven by a steam engine.   Because of the increase in the rate of rise of temperature the loss of heat due to radiation, etc., was a smaller fraction of the total heat than in Joule's experiments.   Consequently, the true rise in temperature, after the cooling correction had been applied, could be obtained more accurately.

(2) Joule's thermometer had not been calibrated against a standard thermometer, and in consequence his rise in temperature had been measured on an arbitrary scale.   Rowland used thermometers which had been compared with a standard constant volume air thermometer, and he was thus enabled to reduce his readings to the absolute scale of temperature.

(3) Joule assumed the specific heat of water to be constant between 0° and 100° C.   Rowland found a minimum value for the specific heat at 29° C.

Rowland's apparatus is shown in Fig. 206.   The calorimeter was supported by means of a vertical shaft *ab,* both shaft and calorimeter being suspended by a torsion wire.   The interior of the calorimeter was of the complicated form shown in Fig. 207.   It contained a large number of vanes, so that the paddle wheel (Fig. 208) could rotate without jerking,

and at the same time offer considerable resistance to the water. The axis of the paddle projected through the base of the calorimeter, and was connected to the shaft *ef* (Fig. 206), which was uniformly rotated by
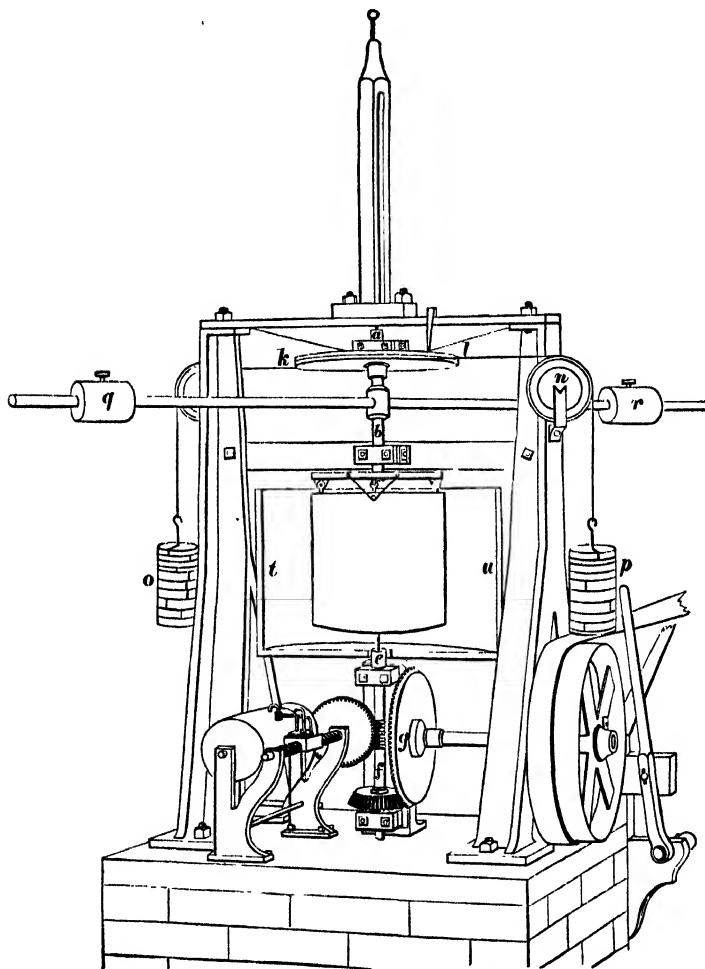

FIG. 206. ROWLAND'S APPARATUS

the steam engine supplying power to the apparatus. The friction of the water tends to make the calorimeter rotate, and produces a couple in the shaft *ab*. This couple is counterbalanced by an equal and opposite couple, due in part to the torsion of the suspending wire but mainly to the action of the weights *op* attached to silk tapes passing round the wheel *kl*. The sliding weights *qr*, attached to the projecting arm, made

it possible to vary the moment of inertia when determining the couple due to torsion. The thermometer necessary to measure the rise in temperature is not shown in Fig. 207, but it was inserted in and protected by a perforated copper tube. A water jacket tu surrounded the calorimeter, and the radiation between them was measured by the method of cooling. The error due to this cause was small.
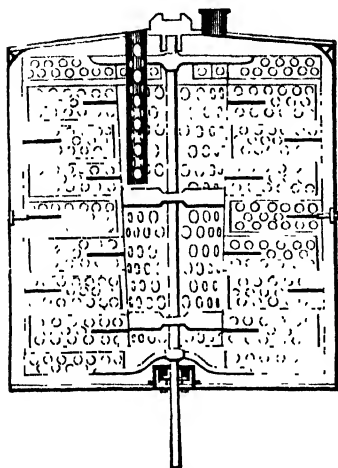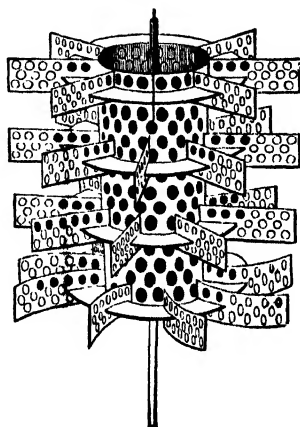

FIG. 207. CALORIMETER IN
ROWLAND'S APPARATUS

FIG. 208. PADDLES IN
ROWLAND'S APPARATUS

Rowland obtained values of the mechanical equivalent of heat at different temperatures between 5° and 35° C. Table 44 gives some of these values, the second column being in gravitational units (grammetres * per calorie) at Baltimore, and the third column being in joules (10^7 ergs) per calorie.

TABLE 44

SOME OF ROWLAND'S RESULTS

Tempera-ture, °C.	Equivalent in gm.-metres/cal.	Equivalent in joules/cal.
5	429·8	4·212
10	428·5	4·200
15	427·4	4·189
20	426·4	4·179
25	425·8	4·173
30	425·6	4·171
35	425·8	4·173

* The gram-metre is the work done in raising one gram through a height of one metre.

Rowland recalculated Joule's 1878 results in terms of the scale of the air thermometer and found that at 14·6° C. Joule's value for the mechanical equivalent was smaller than his own by only 1 part in 550.

In 1895 Schuster in Manchester compared Joule's thermometer with a Tonnelot thermometer standardised at Sèvres, and found as the corrected result of Joule's experiments 1 calorie at 16·5° C. of the nitrogen scale = 4·173 joules.

Reynolds and Moorby's experiments. Some large scale experiments were conducted by Reynolds and Moorby in 1897. A hydraulic brake was attached to the shaft of a triple expansion 100 horse power engine, which made 300 revolutions per minute. There is a continuous flow of water through the brake, and water runs through at such a rate that although it enters at a temperature near 0° C. it comes out at a temperature near 100° C. The work expended on the water is measured by means of a dynamometer, which consists of a lever and weights fastened to the brake.

The results give a numerical value for the mean calorie between 0° and 100° C. of 4·1833 × 10⁷ ergs. These experiments, standing alone, do not give the value of the mechanical equivalent of heat at any one given temperature and therefore cannot be directly correlated with the results of other workers.

Experiments of Laby and Hercus. These experiments, extending over a number of years, were undertaken to determine with the highest precision attainable the *mechanical* equivalent of heat (as distinct from the *electrical* equivalent to be discussed in a later section). In measuring the work done, the principle of Hirn's balance, used by Joule and Rowland, is still employed, and the heat is measured by the method of continuous flow calorimetry. But the production of heat in the calorimeter is brought about, not by mechanical friction, but by an electromagnetic arrangement described as an induction dynamometer.

Experiments were commenced in Melbourne by Laby and Roberts in 1918, and when the latter left Australia in 1920 were continued by Laby and Hercus * who published their results in 1927. Their apparatus is shown diagrammatically in Fig. 209. It consisted of two main parts : (1) the " rotor ", an electromagnet NS, which rotates on ball bearings B_1B_2 about a vertical axis and in so doing produces a rotating magnetic field ; (2) the " stator ", which is also the calorimeter, C. The stator is situated within the rotor and is mounted on ball bearings F and torsion wire Y so as to be free to rotate about the same vertical axis. Its rotation is, however, prevented by means of an applied couple, as in Hirn's balance. It is claimed that the magnitude of the couple, G, could be measured with an accuracy approaching 1 in 10,000. The couple is applied to the

* Laby and Hercus, *Phil. Trans.*, A, Vol. 227, pp. 63-91 (1927).

torsion wheel by means of weights WW hanging on tungsten wires which pass over carefully designed pulleys.

When the copper calorimeter, or stator, is thus held stationary in the rotating magnetic field, currents are induced in it and heat is generated. This heat is measured by the method of continuous flow, for there is a steady flow of water through copper tubes forming part of the stator. The total amount of heat developed in an experiment is calculated after finding the mass of water which passes during the run, and the rise of
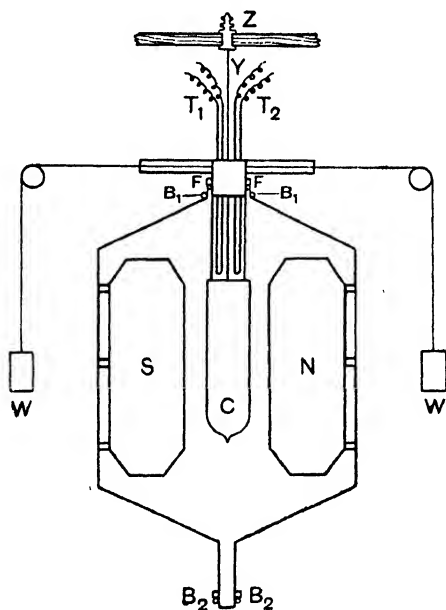
FIG. 209. INDUCTION DYNAMOMETER AND CALORIMETER
(LABY AND HERCUS)

temperature. This rise is the difference between the temperature of the inflowing and that of the outflowing water. It was measured by means of platinum resistance thermometers T_1 and T_2, enclosed in vacuum jackets and connected differentially. To avoid heat loss at the upper end of the stator, the temperature of the room was adjusted to be closely that of the upper end. In this way it is claimed that the heat loss was reduced to only 0·003 per cent.

The energy input to the stator in an experiment is proportional to the mean couple acting upon the stator and to the number of revolutions made by the rotor or electromagnet. The value of the couple is found from measurements of the total suspended mass and the diameter of the torsion wheel, as in the experiments of Joule (1878) and Rowland.

The value of J is calculated from the ratio of the work supplied to the heat given out. To obtain an accurate value, it is essential to ensure that the apparatus is running steadily in all ways, that is to say, the magnetic field, the rate of rotation and the flow of water must all be constant. Laby and Hercus made twenty-three determinations of J by this method, and the weighted mean of their experiments is

$$1 \text{ calorie at } 16 \cdot 7^\circ \text{ C.} = 4 \cdot 1841 \times 10^7 \pm 0 \cdot 0001 \text{ ergs.}$$

Using Callendar's values for the temperature variation of the specific heat of water, this is equivalent to

$$1 \text{ calorie at } 15^\circ \text{ C.} = 4 \cdot 1860 \times 10^7 \text{ ergs,}$$

and $\qquad 1 \text{ calorie at } 20^\circ \text{ C.} = 4 \cdot 1809 \times 10^7 \text{ ergs.}$

2. ELECTRICAL DETERMINATIONS

It is also possible to obtain a value for the mechanical equivalent of heat by an indirect method, when the energy required to heat a certain mass of water is supplied by an electric current, and measured in terms of electrical units. Joule made certain experiments in this direction, but regarded them as less trustworthy than those made by the direct method described above. The accuracy of results obtained by this method depends, however, upon a knowledge of the electrical units, and since these are now known much more accurately than they were in the time when Joule worked, modern electrical determinations of the mechanical equivalent of heat are of the greatest value: When a coil of wire carrying a current is immersed in water, any one of the three following methods may be used to determine the energy spent in raising the temperature of the water :

(1) Measure E, I, and t,
(2) Measure I, R, and t,
(3) Measure E, R, and t.

Here E = electromotive force ; I = current ; R = resistance ; t = time of duration of the experiment.

The simple equations for the electrical energy are

$$A = EIt = I^2Rt = \frac{E^2}{R} t.$$

If we assume the specific heat of water constant and equal to unity, we may say that the heat energy required to raise m gm. of water through θ° C. is $Jm\theta$. Since this heat energy is regarded as equivalent to the electrical energy, A, the " electrical equivalent " of heat, J, is found from the equation $Jm\theta = A$. The value of A is required in absolute units (ergs or joules) consequently it is necessary to know accurately the relation

between the practical (or international) electrical units and the absolute electrical units.

Experiments of Griffiths. In 1893, Griffiths made some experiments using the third method and measured the resistance of a coil of platinum wire heated by means of storage cells and immersed in a calorimeter containing a known quantity of water. The E.M.F. across the terminals of this coil was measured against a standard Clark cell, and the rise in temperature of the water was observed with a mercury thermometer compared with a Callendar-Griffiths platinum thermometer and with a Tonnelot thermometer which had been standardised at the Bureau International. An efficient stirring device was required in the calorimeter, and it was found necessary to employ a large number of corrections.

Griffiths's final value was

$$1 \text{ calorie at } 15° \text{ C.} = 4\cdot198 \times 10^7 \text{ ergs.}$$

Experiments of Schuster and Gannon. Two years later, in 1895, Schuster and Gannon in Manchester used the first method and investigated the heating effect of an electric current by measuring E and I. E was determined as before by comparison with a Clark cell, while the current, or rather the value of It, was measured by means of a silver voltameter.

The final value of these workers was

$$1 \text{ calorie at } 19\cdot1° \text{ C.} = 4\cdot1905 \times 10^7 \text{ ergs,}$$

but it is said that the use of a filter paper to enclose the silver plate of the voltameter led to too large a result.

Experiments of Callendar and Barnes. In 1899 Callendar and Barnes carried out a very accurate determination of the mechanical equivalent of heat, using the first method, and measuring E and I. They employed an experimental method involving a continuous flow of water through a long tube. Their experiments have already been described in detail on p. 182 in the chapter on Calorimetry. The value of the equivalent that they obtained was

$$1 \text{ calorie at } 20° \text{ C.} = 4\cdot180 \times 10^7 \text{ ergs.}$$

Experiments of Jaeger and Steinwehr. A most important series of investigations was carried out by Jaeger and Steinwehr in 1921. These workers claim an accuracy of a few parts in ten thousand. Their measurements were all made electrically. A cylindrical copper calorimeter containing water was heated by means of a coil of constantan wire through which flowed a current of about 10 amperes. This current was measured accurately by passing it through a standard 0·1 ohm resistance in series with the heater, and measuring the potential drop on this with

a potentiometer against a standard Weston cell. The fall of potential across the ends of the heating coil was measured in a similar manner. The rise in the temperature of the water in the calorimeter was measured by means of a standard platinum thermometer.

. Jaeger and Steinwehr considered that their apparatus included the following advantages :

1. They used a large mass of water (50 kgm.), thus enabling them to make the water equivalent of the calorimeter and other metal fillings only a little over 1 per cent. of the total mass of water.

2. They used a small temperature rise (1·4° C.), thus ensuring that Newton's law of cooling is strictly applicable in determining the cooling correction. A disadvantage in this is that the temperature measurements have to be made very accurately to avoid a large percentage error in the final result.

3. They obtained efficient stirring of the water in the calorimeter.

4. They arranged that the temperature of the surroundings was well defined by placing the calorimeter inside a double-walled metal box. The space between the walls of this box was filled with water, and this was kept at a constant temperature.

When the apparatus was working, each experiment lasted for six minutes. About seventy experiments at temperatures ranging from 5° to 50° C. were made ; in each case the actual rise in temperature observed was small.

The final value obtained for the electrical equivalent of heat was

$$1 \text{ calorie at } 15° \text{ C.} = 4·186 \times 10^7 \text{ ergs.}$$

THE MECHANICAL EQUIVALENT OF HEAT

Joule's equivalent : accurate value in various units. Since the mechanical equivalent of heat expresses the relation between a certain number of units of work and the corresponding number of units of heat, it is clear that any convenient unit may be chosen for measuring the amount of work and likewise any convenient unit for expressing the corresponding amount of heat. As the question of change of units frequently arises, it is desirable to consider carefully how the value of J is affected by a change from one set of units to another. This is best understood by considering some important examples (see Chapter XII, Part I).

The value of J found by Joule was about 772 foot-pounds per British Thermal Unit, but later investigations have shown that the true value is nearly 778. We shall assume the value (which is easy to memorise)

$$J = 777·7 \text{ (foot) (pound) (degree Fahrenheit).}$$

It should be noticed that this refers to the latitude of Greenwich and to the standard temperature 60° F.

(It may be remarked that 59° F. is the same as 15° C., so that the 15° calorie recommended by the International Union of Physics may conveniently be introduced without appreciable error arising.)

The fundamental thermometer interval contains 180 Fahrenheit degrees but only 100 Centigrade degrees. That means that the Fahrenheit degree is smaller than the Centigrade degree in the ratio 5 to 9. Thus 777·7 (foot) (pound) (degree Fahrenheit) must be *multiplied* by 9/5 to convert to the Centigrade scale, giving $777·7 \times \frac{9}{5} = 1399·9$, or nearly

$$1400 \text{ (foot) (pound) (degree Centigrade)}.$$

The unit of mass does not affect the numerical value of J for it is used alike both in the unit of work and in the unit of heat.

The unit of length does, however, modify the result. Since one foot is equal to 30·48 cm. we must *multiply* by 30·48 to obtain the result in (cm.) (gram) (degree Centigrade) units. Thus we find

$$J = 426400 \text{ (cm.) (gram) (degree Centigrade)}$$
$$= 426 \text{ (metre) (gram) (degree Centigrade)}.$$

To obtain the value in dynamical units of work (ergs) we have to multiply by 981·17, the value of g at Greenwich. This gives

$$J = 4·184 \times 10^7 \text{ (erg) (degree Centigrade)}$$
$$= 4·184 \text{ (joule) (degree Centigrade)}.$$

Summary of experimental determinations. The values of Joule's equivalent, J, are given in joules (10^7 ergs) per 20° calorie.

Direct Determinations.		*Indirect Determinations.*	
Joule, 1843	4·169	Griffiths, 1894	4·190
Rowland, 1880	4·182	Schuster and Gannon, 1896	4·190
Reynolds and Moorby, 1897, from *mean* cal.	4·176	Callendar and Barnes, 1909	4·180
		Bousfields, 1911	4·177
Laby and Hercus, 1927	4·181	Jaeger and Steinwehr, 1921	4·182

The 15° calorie is about 1 part in 1000 greater than the 20° calorie.

Birge gives $$\frac{J_{20}}{J_{15}} = 0·999058.$$

The results of experiments for determining the " electrical equivalent " of heat are only comparable with those on the " mechanical equivalent " in so far as the *absolute* values of the electrical standards (ohm, ampere and volt) are known. Much work has been done on the determination of the International (or practical) electrical units in absolute measure, and it is probable that the accuracy with which they are known is con-

siderably greater than the accuracy with which J can be found by direct experiment.*

The values of the fundamental physical constants have been discussed by Birge in an important paper,† published in 1929.   In this paper Birge gives two values for Joule's equivalent, one deduced from dynamical experiments, the other from electrical experiments.   They are:

Mechanical equivalent of heat :

$$J_{15} = 4\cdot1852 \pm 0\cdot0006 \text{ abs. joule cal.}_{15}^{-1}.$$

Electrical equivalent of heat :

$$J'_{15} = 4\cdot1835 \pm 0\cdot0007 \text{ int. joule cal.}_{15}^{-1}.$$

In another section of his paper he says :

$$1 \text{ int. joule} = 1\cdot00041 \pm 0\cdot00010 \text{ abs. joule,}$$

so that the two results (for J and J') are in very close agreement.

Laby and Hercus ‡ have made further investigations as to the accurate value of the mechanical equivalent of heat.   After discussing the effect of the aeration of the water used in the determination, they conclude that the value calculated by Birge,

$$4\cdot1852 \times 10^7 \text{ ergs per cal. at } 15^\circ \text{ C.,}$$

is to be accepted.

QUESTIONS

CHAPTER XXV

1. Discuss the differences involved between the direct and indirect methods for the accurate determination of the mechanical equivalent of heat, and point out the reasons why Joule considered the former methods would yield the more accurate value.   Do his objections to the use of the indirect methods still hold good?

2. What do you understand by the term *friction balance?*   Describe how an apparatus involving this conception has been employed to determine Joule's equivalent accurately.

3. Describe carefully any one *accurate* method of determining Joule's equivalent (such as the method of Laby and Hercus), mentioning the chief difficulties met with in the method selected.   (St. A. U.)

4. What is meant by the expression *the electrical equivalent of heat?*   Describe the experiments of Jaeger and Steinwehr on the accurate measurement of this constant.

* Laby, *Proc. Phys. Soc.*, Vol. 38, p. 169, 1926.

† Birge, *Reviews of Modern Physics* (*Phys. Rev. Supplement*), Vol. I, 1, 1929.

‡ Physical Society, June 21, 1935.

CHAPTER XXVI

MATHEMATICAL FORMULATION OF THE FIRST LAW

CENTURIES of human experience have verified the fact that it is impossible to obtain perpetual motion. This principle may be stated more accurately as follows (Planck) :

It is impossible to construct an engine which will work in a *cycle* and produce continuous work, or kinetic energy, from nothing.

This applies to all kinds of devices which have been submitted, directly or indirectly, to test, whether they depend on mechanical, thermal, chemical or electrical methods.

This is one way of stating the principle of the conservation of energy, which includes the first law of thermodynamics as a particular case. A formal statement of this law may be given in these words :

If a body or system undergoes any cycle of operations (such that the initial state and the final state are the same), the total amount of heat taken in by the system from external bodies is proportional to the amount of work done by the system on external bodies. Each of these amounts is to be reckoned algebraically, that is, with due attention to sign, throughout the whole cycle of operations.

Conservation of energy. The investigations of Joule proved that the heat developed when mechanical energy is destroyed is always exactly proportional to the energy that thus disappears. This leads us to the conclusion that heat itself is a form of energy. We recognise other forms also, such as chemical energy, electrical energy, or radiant energy. The principle of transmutation of energy is that energy may be converted from one form to another, but, as there is always strict proportionality between the quantities, the energy of the first form may be regarded as the equivalent of the energy of the second form. This leads to a more exact statement of the principle of conservation of energy. In these transmutations of energy no energy is destroyed, and consequently the energy of a self-contained system is a fixed and constant quantity. The qualification that the system should be self-contained is of great importance—it implies that the system can be completely isolated from its

surroundings.   If any energy be allowed to enter the system from without or to leave it and pass to the external world, we can no longer assert that the energy of the system remains constant.   This condition limits very considerably the application of the principle.   Some philosophers have tried to escape from the difficulty of conceiving a self-contained system, by extending the principle to the whole universe, stating that the sum total of the energy in the universe is constant.   But as we have no means of testing such a statement it seems useless to make such a generalisation. The difficulty as to the system being self-contained is not usually serious in an actual experiment, which should be arranged in such a way that transferences between the system and its surroundings are reduced to a minimum.   It is generally possible to make allowances for any such small additions or subtractions of energy.

Conservation of energy is the basic principle of modern physics, and in spite of some difficulties which have arisen in experiments on the atomic nucleus it is generally regarded as applicable on the microscopic as well as on the macroscopic scale.

It is important to observe that in the measurement of energy only *differences* are actually measured.   It is often convenient to adopt some standard for zero energy, but such a standard is usually *arbitrary*.   An analogy is found in measuring the height of a body.   In this case we select some arbitrary level as our starting-point or zero level, as for instance in stating the height of the body above sea level.   The *sign* to be attached to a quantity of energy is a matter of convention and definition.   Sometimes we shall find it convenient to think of the energy as a *positive* quantity when it is *possessed or received by* the particular body or system considered, but at other times it may be convenient to give the positive sign to the energy which the system communicates to the surroundings.   To borrow the phraseology of financial matters it is a question of bookkeeping.   Here we distinguish between debit and credit, between income and expenditure, between imports and exports.   In this connection the phrase *invisible* exports may be regarded as significant.

Heat engines.   From the standpoint of the engineer, thermodynamics is chiefly concerned with the process of getting mechanical work done through the agency of heat.   Any machine for doing this is called a **heat engine.***   Another important practical process is that of cooling bodies to a temperature below that of their surroundings, or of removing heat from bodies already colder than their surroundings.   Any machine for doing this is called a **refrigerating machine.**   The action of such a machine is the reverse of that of a heat engine.

In any heat engine heat is supplied to the engine at a high temperature,

* Ewing, *Thermodynamics for Engineers* (Cambridge).

and the engine discharges heat at a lower temperature.   The steam engine affords a good example ; in this case heat is taken in at the temperature of the boiler, heat is discharged at the temperature of the condenser. The former quantity is greater than the latter, and the difference (in part at least) is converted into the work done by the engine.

In a refrigerating machine heat is taken in at a low temperature, and heat is discharged at a high temperature. But the latter quantity is greater than the heat taken in, for the work spent in driving the machine is converted into heat, and thus heat has to be discharged at the higher temperature.   Such a machine might be spoken of as a **heat pump**.

As the action is the converse of that previously considered, we may use the term heat engine to include both types of machine.

Working substance.   In any heat engine there is always some working substance " which forms the vehicle by which heat passes through the machine ".   This substance must be able to take in heat at a particular temperature, and to give it out at some other temperature.   In the process of conveying heat from one level of temperature to another the size or volume of the material changes, and it is because of this *change in size* that work is either done *by* the working substance or is done *upon* it.

We have seen in Chapter XVI that, when considering a gas, the work done may be represented by using a graphical method.   This method is of general application, and is so important in thermodynamics that, even though some repetition is involved, we shall consider it in detail. The treatment is applicable to any working substance, whether fluid or solid.

The indicator diagram.   The theory of heat owes a great deal to the interaction between theoretical considerations and the practical application of scientific results.   The development of the steam engine, in particular, has led to important advances in theory.   One illustration of this interplay is afforded by the **indicator diagram** introduced by James Watt.   The original " indicator " measured the *pressure* of the steam, but later the apparatus was modified so as to show both pressure and volume on a chart.   This diagram gives a graphical representation of the condition of the steam or other working substance in the cylinder of a heat engine.   On the chart we plot the relation between pressure and volume, pressure being plotted along the vertical axis and the volume along the horizontal axis.   We may imagine the cylinder placed with its axis horizontal so that the closed end of the cylinder coincides with the origin of coordinates, and the position of the piston determines the volume (Fig. 210).   We may, for convenience, assume the area of cross-section to be unity, so that the distance ON between the fixed end and the piston is numerically equal to the volume.   Corresponding to this

particular volume ON there will be a definite pressure AN; then the point A represents the condition of the working substance with regard to these
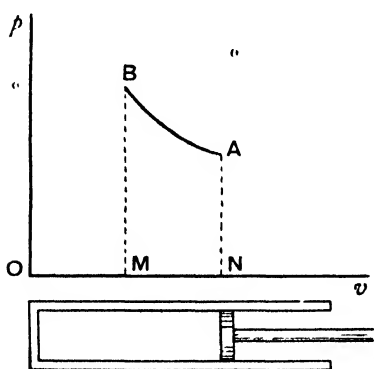

FIG. 210.   INDICATOR DIAGRAM

two variables. Three variables, p, v and θ (θ being the temperature on *any* chosen scale), are required to specify completely the condition of the substance, but these three variables are connected by an equation which is called the "characteristic equation" or the "**equation of state**", the most familiar illustration being the gas equation, $pv = RT$, in which we use the gas scale of temperature and put T for θ. Another familiar equation of state is the equ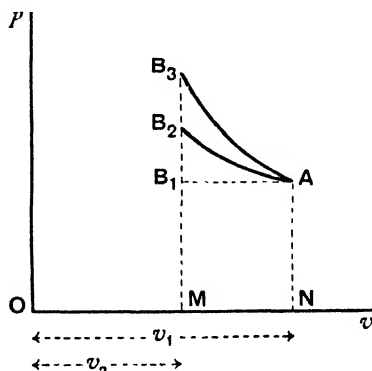ation of van der Waals. By means of the characteristic equation one of the three variables may be expressed in terms of the other two. It is assumed that we are working with a fixed mass of material.

In the theory of heat we have to consider a change from one state of the working substance to a second. When a substance passes from a state indicated by A to a state indicated by B on the $p-v$ diagram, the changes it undergoes in the processes are shown by a curve joining A to B.

Simple illustrations are afforded by (1) a change of volume at constant pressure (an isopiestic change), (2) a change of pressure at constant volume (an isochoric change). In general, both pressure and volume change.

For example, we may suppose that a change takes place from the state represented by A (Fig. 211) corresponding to volume v_1, where $ON = v_1$, to some second state corresponding to volume v_2, where $OM = v_2$. If, as in the diagram, we are considering a compression of the working substance v_2 is less than v_1. There are an infinite number of ways in which this compression may take place, for we may select *any* point, such as

FIG. 211.   ISOTHERMAL AND ADIABATIC CHANGES

B_1, B_2, or B_3, on the ordinate passing through the point M. There are two particular types of change of great importance.

Isothermal and adiabatic changes. First we consider an **isothermal** change; in such a change the temperature of the system is kept constant and the heat produced in compressing the fluid is allowed to pass out through the walls of the containing vessel. Such an isothermal compression is represented, say, by AB_2. The second important type of change is called **adiabatic**. In an adiabatic change no heat is communicated to, or abstracted from, the substance by external bodies. We might·picture the change as taking place in a cylinder provided with walls of non-conducting material, so that no heat can pass through them in either direction. Or, again, if the change is a very sudden one, there will be no time for any appreciable transference of heat. This is illustrated in the compressions and rarefactions occurring in a sound wave, which must be regarded as adiabatic changes (Laplace).

An adiabatic curve will be steeper than an isothermal curve, and we might take AB_3 in the diagram to represent the adiabatic passing through the point A. The change from the point A to the point B_3 may be considered as taking place in two stages. First we suppose an isothermal change occurs from A to B_2, and then we imagine a change follows at constant volume. As the first change is a compression at constant temperature, heat is generated and is given to the surrounding bodies. Now let us suppose that this heat is restored to the substance, keeping the volume constant. The result must be an increase in pressure, i.e. the final point B_3 must be above B_2. Thus the adiabatic AB_3 is steeper than the isothermal AB_2.

Work done in a change. It is important to be able to estimate the amount of work done in any change of the system. Let us suppose that the condition of the working substance is determined by two variables p and v. When the piston (Fig. 212) is forced inwards through a small
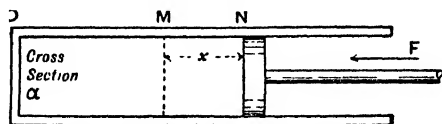

FIG. 212.   WORK DONE IN COMPRESSION

distance the fluid is compressed and work is done by the agent forcing in the piston.

Let α = area of cross-section of cylinder.

x = distance through which piston moves under the action of a *constant* force F.

By definition, pressure is measured as force per unit area, that is, the pressure

$$p = \frac{F}{\alpha}, \quad \text{or} \quad F = p\alpha.$$

The work done, A, in the displacement is the product of the force F and the displacement.

$$A = \text{work done} = F \times x.$$
$$= p\alpha x$$
$$= p \text{ (change in } v)$$
Hence $\delta A = p \, \delta v$ for a *small* change in volume δv.

In the limiting case, when $\delta v \to 0$, we may write for an *infinitesimal* change, $dA = p \, dv.$

When the pressure does *not* remain constant in the process, the work done must be found by integration, and is given by

$$A = \int p \, dv.$$

These results may conveniently be represented on the indicator diagram (Fig. 213 (a)). We have seen that δA the work done in a *small*
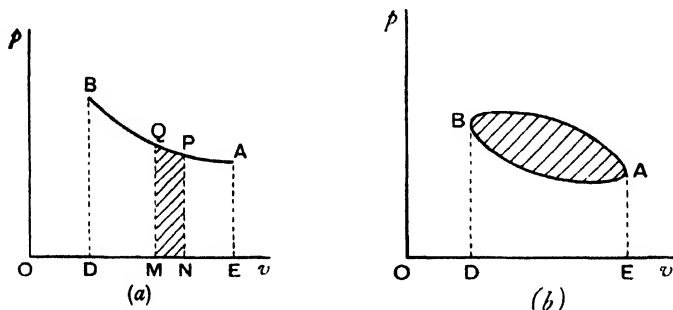
FIG. 213.   REPRESENTATION OF WORK DONE

change of volume is $p \, \delta v$. But p is represented by PN or QM, which only differ by a very small amount, and δv is represented by MN. Hence δA the work done in this small change is represented on the indicator diagram by the *area* of the strip $PQMN$.

When the pressure does not remain constant the work done in a finite change from E to D is

$$A = \Sigma p \, \delta v$$
$$= \text{sum of strips such as } PQMN$$
$$= \text{area } ABDE.$$

The amount of work is represented on the indicator diagram by the area underneath the curve joining the initial and final points.

In a **cyclic change**, a little consideration will show that the work done in the cycle is equal to the area of the cycle. For in the case above, that of compression, work is done *on* the working substance; in expansion, when the piston moves outwards, work is done *by* the working substance,

and the net amount of work corresponds to the difference of the areas underneath the two portions of the curves, that is, to the area of the complete cycle (Fig. 213 (b)).

In estimating the amount of work represented by means of an indicator diagram care must be taken to consider the units employed. The simplest case is that in which, using C.G.S. units, the pressure is in dynes per sq. cm. and the volume is in cubic centimetres. The work done will then be in dyne-cm. units or ergs. But in many instances other units may be more convenient, and in all cases the scale employed for representing pressure and volume must be taken into account in determining the area.

In chemical investigations it is sometimes convenient to measure the pressure in atmospheres and the volume in litres. The product pv is then expressed in litre atmospheres. Since a pressure of 1 atmosphere is about $1 \cdot 013 \times 10^6$ dyne cm.$^{-2}$ the litre atmosphere is about $1 \cdot 013 \times 10^9$ erg.

Generalisation for any mass of fluid.   It should be noticed that this expression for the work done when the volume of the working substance is changed, holds good whatever may be the shape of the receptacle in which the substance is contained. The material need not necessarily be enclosed in a cylinder, but may occupy a region of any shape (Fig. 214).

Let S represent the surface bounding the fluid in its initial condition, the external pressure to which it is subjected being assumed constant all over the surface. Now suppose the fluid expands by a small amount, doing work against this steady pressure in the process. The new surface is indicated by the dotted line S'. We may suppose the original surface divided up into small elements such as AB, of area δS. If we draw normals outwards from each point on the boundary of this element we can picture $ABCD$ as a small cylinder to which the previous argument is applied. The work done in the expansion so far as this element is concerned will be equal to the product of the pressure p and the volume of the element $ABCD$. For the whole surface, the work done will be the sum of such quantities, that is, it will be equal to the product of p and the volume contained between S and S'. Thus we may write as before for the work done $A = p \times \delta v$, where δv represents *the volume between S and S'*.

FIG. 214.   EXPANSION OF A MASS OF FLUID

In this general form the argument may be applied, say, to a cloud, or to any isolated region in the atmosphere, provided the condition that the pressure has the same value all over the surface enclosing the region is fulfilled. It is tacitly assumed that the expansion takes place so slowly that no kinetic energy is developed, and it should be noticed that to make expansion possible the pressure exerted by the substance must be greater than the external pressure by an infinitesimal amount.
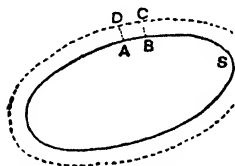
FORMULATION OF THE CONSERVATION PRINCIPLE

Internal or intrinsic energy. The principle of the conservation of energy leads to the conclusion that a body or system in a given state possesses, in addition to the *visible* kinetic energy, **internal** or **intrinsic energy.** We use the symbol U to denote **internal energy.** This internal energy depends on the configuration of the system and on the motion of the molecules. It may be regarded as partly potential energy arising from attraction between the ultimate particles and partly kinetic arising from the invisible motion of the particles. As we are ignorant of the exact molecular constitution of the system we cannot ascertain the ultimate fate of any heat it may absorb. I⁺ may be that in the last analysis all the energy is of the type of kinetic energy.

Let the system *take in* a quantity of heat represented by Q, measured in units of work, and let it perform A units of *external* work in the change from one state to another. It is to be noticed that Q (sometimes called the " heat entry ") is the heat transferred across the boundary *to* the system either by thermal conduction or by radiation. These are the only methods by which such transference can take place. Then $Q - A$ represents the excess of the energy supplied in the form of heat over the external work done, and in accordance with the principle of the conservation of energy (assuming that there is no change in the *visible* kinetic energy of the system) this must be equal to the change in the internal energy, that is,

$$Q - A = U_2 - U_1,$$

where U_1 and U_2 are the internal energies before and after the change, i.e. U_1 is the intrinsic energy in the *first* state, U_2 the intrinsic energy in the *second* state. This equation is really a definition of the quantity $U_2 - U_1$, or ΔU the *finite* change in U, on the right-hand side. The equation may be expressed by saying :

heat taken in by system − external work done by it
= increase of internal energy.*

This result may be stated with reference to a *small* change in the state of the system by taking δQ to represent the small amount of heat communicated to the system and δA the small amount of external work done. Then the difference between δQ and δA corresponds to a small *increase* δU in the internal energy, so that

$$\delta Q - \delta A = \delta U.$$

One other result of great importance as to the change in the internal

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* It should be noticed that Nernst in his book *Theoretical Chemistry* takes the *negative* value of U to denote the content of energy.

energy of a self-contained system must be stated here. Let us fix our attention on two particular states of the system, each state being definite.

When the system passes from one state to another the change in the *internal* energy is *independent of the path* between the two states. Here the term " path " is used to describe a continuous series of infinitesimal changes by which the system is brought from its initial to its final state.

It will be noticed that the symbol **δ** before U on the right-hand side of the above equation is in black face type. This is to draw attention to the fact just mentioned as to the nature of U.

Illustration by means of an indicator diagram. These general statements become clearer when a particular case is considered. We suppose a definite mass of some " working substance " (steam, for example) is enclosed in a cylinder of uniform cross-section by a piston. We represent the state of the substance as regards pressure and volume by using an indicator diagram. Let a finite change take place from a condition represented by a point A (Fig. 213) to a condition represented by a point B through a series of states corresponding to points on the curve or *path AB*. Then, as we have seen, the work done is represented by the area underneath the curve AB, for this area gives the value of

$$\int_A^B p \, dv.$$

Taking A and B on the indicator diagram to represent two specified states of the system, we may pass from A to B by any number of different routes, but the difference between the internal energy at A and B is independent of the particular route followed. We shall denote the difference between the internal energy in any state and that in some standard state by U. In practical work we are only concerned with *changes* in energy and not with the absolute value of the energy. This means that we can choose the standard state to suit the problem in hand.

It must be understood that in the limit **d**U is the differential of a function U of the variables which determine the state, but δQ and δA are not differentials of functions Q and A, as such functions do not exist. We have seen that for a simple substance the work done $= \int_{v_A}^{v_B} p \, dv =$ area $ABDE$, and this area depends on the path from A to B. It follows that the heat taken in also depends on the path from A to B. We may pass from this differential form of the expression to a finite change by a process of summation, and write the result in the form :

$$\Sigma \delta Q - \Sigma \delta A = \int dU = U_2 - U_1.$$

The term **perfect differential** is used by mathematicians when the change from one state to another is independent of the particular (infinitesimal) path between those states. This is discussed more fully on page 649. When we wish to emphasise the fact that **d**U is a perfect differential black face type will be used.

APPLICATIONS OF THE FIRST LAW

The equation $Q - A = U_2 - U_1 = \Delta U$ may be regarded as the fundamental relation expressing the first law of thermodynamics.

It expresses the relation between the heat Q *supplied to* the working substance, the external work done, and the change in the intrinsic energy in passing from the first state to the second.

It may also be written for a small change as

$$\delta Q - \delta A = \delta U.$$

Heat absorbed at constant volume and at constant pressure. There are two important cases which arise in practice.

1. *Heat absorbed at constant volume.* No external work is done when no change in volume takes place, that is,

$$A = 0.$$

Consequently the heat absorbed is

$$Q_v = U_2 - U_1 = \text{increase of intrinsic energy.}$$

2. *Heat absorbed at constant pressure.* In this case

$$\begin{aligned}
Q_p &= (U_2 - U_1) + A \\
&= U_2 - U_1 + p(V_2 - V_1) \\
&= (U_2 + pV_2) - (U_1 + pV_1) \\
&= H_2 - H_1
\end{aligned}$$

where $\quad\quad H = U + pV.$

The heat absorbed at constant pressure is equal to the increase in H.

The function H is called by engineers the " total heat ", or the " heat content ". A. W. Porter remarks that these names are " survivals from old caloric days. Since H does not measure heat in general, neither of the names is appropriate, and both are liable to lead to confusion." The function H is the same as the " heat function at constant pressure " (Gibbs) or the " enthalpy " (Onnes). It is to be noted that dH is a perfect differential. The **enthalpy** H is of special importance because so many thermal processes take place at atmospheric (that is, at constant) pressure.

Specific heat. We start once more from the equation $\delta Q - \delta A = \delta U$, which defines the intrinsic energy. This may be written $\delta Q = \delta U + \delta A$, an equation expressing the fact that the heat communicated may be employed in increasing the intrinsic energy and in doing external work. Suppose we are dealing with *unit mass* of substance. Let a small quantity of heat δQ be supplied to the substance and be absorbed. In general, the temperature is in consequence raised from θ to $\theta + \delta\theta$. We

consider the ratio of δQ to $\delta\theta$ and proceed to the limit when $\delta\theta$ becomes infinitesimal. This is expressed in mathematical language as

$$\underset{\delta\theta \to 0}{\mathrm{Lt}} \frac{\delta Q}{\delta\theta} = \frac{dQ}{d\theta}.$$

Then $\dfrac{dQ}{d\theta}$, which represents this limiting ratio, is called the *specific heat* of the substance at the temperature θ. This specific heat we denote by C, so that

$$C \equiv \frac{dQ}{d\theta}.$$

We may notice that the unit mass may be either one gram or one gram-molecule.

It is sometimes convenient to use the symbol c for the heat capacity per gram, and C for the heat capacity per gram-molecule.

It is important to notice that there may be any number of values for C corresponding to the conditions under which the change takes place. There are two important particular cases which deserve special mention.

(1) When the *volume* of the substance is kept constant.
The **specific heat at constant volume** is

$$C_v \equiv \left(\frac{dQ}{d\theta}\right)_v.$$

(2) When the *pressure* is kept constant.
The **specific heat at constant pressure** is

$$C_p \equiv \left(\frac{dQ}{d\theta}\right)_p.$$

The expressions above are the strict mathematical definitions of these specific heats. In practice we often take the rise of temperature to be $1°$ C., so that, for example, the specific heat at constant volume is the quantity of heat required to raise the temperature of unit mass of the substance by $1°$ C. when the volume is kept constant. A similar definition may be given for C_p.

In the former case the pressure increases whilst the volume is kept constant, and no external work is done. In the latter case the volume increases under constant pressure, and an amount of external work is done which is measured by the product of the pressure and the change of volume. Consequently $C_p > C_v$. We shall show that for a perfect gas $C_p - C_v = R$, where R is the gas constant.

The ratio of C_p to C_v is usually denoted by γ and may be determined experimentally in a number of different ways. For dry air the value is very near to $1 \cdot 402$, for oxygen it is $1 \cdot 400$, and for monatomic gases it is $1 \cdot 667$.

Heat absorbed by any mass in a finite change of temperature. For any mass m of the substance, the heat absorbed when the temperature is raised by a small amount $\delta\theta$ is given by

$$\delta Q = mc\,\delta\theta.$$

Here m is the mass in grams and c is the thermal capacity per gram (specific heat).

For a *finite* rise in temperature from θ_1 to θ_2, the heat absorbed would be

$$Q = \int_{\theta_1}^{\theta_2} mc_\theta\,d\theta = m\int_{\theta_1}^{\theta_2} c_\theta\,d\theta,$$

where we write the specific heat as c_θ to indicate that it is a function of the temperature, or $c_\theta = f(\theta)$.

The evaluation of the integral depends on a knowledge of the variation of c with θ, that is, on a knowledge of the form of the function $f(\theta)$.

We may, however, write $\quad Q = m\bar{c}(\theta_2 - \theta_1)$

in dealing with a finite change of temperature, where $\bar{c}$ is the **mean specific heat** for the temperature interval θ_1 to θ_2. This equation is really a *definition* of $\bar{c}$.

Latent heat. It is sometimes found that heat is supplied to a substance without any change of temperature taking place. This happens when there is a change in the state of aggregation of the substance. Thus in the liquefaction of ice at $0°$ C. heat is absorbed by the ice from some external source, and the temperature remains at $0°$ C. until all the ice has melted. The amount of heat supplied may be measured by the fall of temperature of some body giving out the heat, as in the ordinary method in which warm water is placed in contact with the ice, or the energy may be derived from an electric current passing through a resistance coil. In such a case, since there is no observed change of temperature, the heat supplied is said to become latent and is called **latent heat** (Joseph Black). The **latent heat of fusion** L_f (or the **heat equivalent of fusion**) is the amount of heat required to change unit mass of the substance from the solid to the liquid state without change of temperature.

The **latent heat of evaporation** L_e (or the **heat equivalent of evaporation**) is the amount of heat required to change unit mass of substance from the state of liquid to the state of vapour without change of temperature.

Heat of reaction. When substances are mixed together, or go into solution, or take part in a chemical reaction, it is found in general that the process is accompanied by the evolution or absorption of heat. This quantity of heat we call the **heat of reaction** of the process under consideration.

It is customary for chemists to reckon the heat of reaction as *positive* when heat is set free or developed (**exothermic process**), as *negative* when heat is absorbed or rendered latent (**endothermic process**).

This convention differs from that we have adopted previously (p. 562) and is liable to cause confusion.   Some authors (e.g. Partington, *Chemical Thermodynamics*, p. 22) get over the difficulty by using *block* letters for heats of reaction, ordinary letters for quantities of heat defined as the heat *absorbed* in a change.

Many chemical reactions are accompanied by the **evolution of heat,** in some cases by active combustion, as in the familiar instance of the combustion of coal.   Thus chemical energy may be set free in the form of heat (or electrical energy).   The heat evolved represents the difference between the energies of the system before and after the change has taken place.   As an illustration of an **exothermic process**, in which evolution of heat takes place, we take the union of hydrogen and chlorine to form one molecule of HCl, $H + Cl = HCl + 22$ kg. cal.

Here the **molecular heat of formation** is 22 kg. cal., this being the heat liberated when the molecular weight in grams is formed from the elements H and Cl.   Hydrochloric acid is an exothermic compound formed from hydrogen and chlorine with evolution of heat, i.e. loss of energy.

When absorption of heat occurs, we speak of an **endothermic process.** The thermochemical equation

$$HCl\ Aq + 3O = HCl\ O_3 - 15\ \textbf{kg. cal.}$$
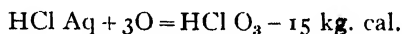
represents the fact that the formation of chloric acid is accompanied by absorption of heat.   Chloric acid is an endothermic compound and contains more energy than its constituents.   Such compounds are unstable and tend to disintegrate.

It is necessary to distinguish between heats of reaction at constant volume and heats of reaction at constant pressure.   We shall return to this point later.

Some values of the molecular heat of formation for various inorganic compounds are given in Table 45.*

TABLE 45

MOLECULAR HEAT OF FORMATION

Compound	Molecular heat of formation in kgm.-cal.
HCl (gas)	22
HBr (gas)	8
HI (gas)	-6
P_2O_5 (solid)	369
H_2SO_4 (liquid)	193
CS_2 (gas)	-19
HCN (gas)	-30

* For values for other substances see Kaye and Laby, *Tables of Physical and Chemical Constants*, pp. 65 and 66 (1936).

In 1937 a British committee representing both physics and chemistry recommended a change in the then prevailing sign convention, so that the heat of reaction has a positive value for an endothermic reaction and a negative value for an exothermic reaction. The committee advocated the use of the symbol ΔH for the heat of reaction at a constant pressure of 1 atmosphere and ΔU for the heat of reaction at constant volume.

The Law of Hess. The heat evolved or absorbed in a chemical change depends only on the initial and final states and is independent of the intermediate states when the volume is constant and also when the pressure is constant. This law is in accordance with dU and dH being perfect differentials where $Q_v = U_2 - U_1$ and $Q_p = H_2 - H_1$. The applications of the law of Hess in physical chemistry are of great importance. Although the law is only strictly true under the conditions stated, it is valid approximately in all reactions between solids and liquids because Q_v and Q_p are then very nearly equal.

QUESTIONS

CHAPTER XXVI

1. Write a short essay on the Law of Conservation of Energy.

2. From a consideration of the first law of thermodynamics, derive an expression for the enthalpy of a substance in terms of its pressure, volume and intrinsic energy.

3. Show that the work done on one gram-molecule of a perfect gas in compressing it reversibly from a volume V_1 to a volume V_2 is

$$W = R_M T \log (V_1/V_2).$$

4. Define the expressions *endothermic process* and *exothermic process*. How would you find the heat of reaction when hydrogen and chlorine unite to form hydrochloric acid?

5. If c_p and c_v are the specific heats at constant pressure and constant volume respectively, and u is the internal energy of unit mass, prove that in dynamical units

$$c_v = \left(\frac{du}{d\theta}\right)_v \quad \text{and} \quad c_p = \left(\frac{du}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)$$

CHAPTER XXVII

THE PROPERTIES OF GASES

The properties of gases—actual and ideal. Many of the properties of gases have been described in Part I, but it will be advantageous at this stage to recall some of the more important characteristics of the gaseous state. The comparative simplicity of this state as pictured in the kinetic molecular theory renders is specially suitable for abstract reasoning such as we meet with in thermodynamics. At the same time we must remember that the generality of thermodynamic reasoning is one of its most valuable features, and we are by no means restricted to applying such reasoning to gases.

From the experimental standpoint the most significant properties of a gas are its power of expanding so as to occupy the whole of the vessel in which it is contained, and the fact that by reducing the size of the vessel it can be compelled to occupy a smaller space. These properties of expansibility and compressibility are closely related to the *pressure* exerted by the gas on the walls of the containing vessel. The volume occupied by a given mass of gas depends not only on its temperature but also on the pressure to which it is subjected.

The gas laws. The two laws which sum up the behaviour of gases as regards the relations between pressure, volume and temperature are familiar. They are the law of Boyle and the law of Charles.

BOYLE's LAW. The volume v of a given mass of gas varies inversely as the pressure p, provided the temperature remains constant.

LAW OF CHARLES. The relative expansion between the ice-point and the steam-point is the same for different gases. By the relative expansion is meant the ratio of the increase in volume to the original volume at the ice-point.

A similar statement applies to the pressure of a gas.

These laws are based on experiments carried out with actual gases, and are only approximately true.

DALTON's LAW. As a further experimental result we may add Dalton's law, or the law of partial pressures, according to which the pressure when a number of gases which do not react upon one another are placed in the same vessel, is the sum of the pressures which each would separately exert in the same space.

Density of a gas. Another important property of a gas is its **density.**

In speaking of the density of a gas or vapour it is necessary to distinguish between the absolute and the relative density.

(1) The **normal density,** or simply the **density,** is the mass of unit volume measured under standard conditions of temperature and pressure. By chemists this is often expressed as the weight in grams of 1 litre (or 1000·027 c.c.) of the gas, or vapour, measured at a temperature of 0° C. under standard pressure defined as that due to 76 cm. of mercury.

(2) The **relative density** is the weight of any volume of the substance divided by the weight of an equal volume of pure hydrogen, measured and weighed under the same conditions. Densities are often given relative to that of oxygen (O = 16) at 0° C. and a pressure of 76 cm. of mercury.

As the pressure becomes smaller, the deviations from Boyle's law become less and less, and may be regarded as negligible at very small pressures. It may be assumed that, as the pressure tends to zero, the ratio of the *limiting densities* * ($p \to 0$) gives the exact ratio of the molecular weights (D. Berthelot, 1899).

Gas scale of temperature. As we have shown on page 48, it is possible to construct a gas thermometer which can be used at constant pressure, and in such a case the temperature t measured from the ice-point is *defined* by the equation $v_t = v_0 (1 + \alpha t)$

where α has been found by experiment to be 0·003665 or approximately $\frac{1}{273}$.

Such a thermometer is not entirely suitable for use as a standard, and for many years the practical *standard* scale was that of the constant volume hydrogen thermometer. On this scale the temperature t, measured from the ice-point as zero, is *defined* by the equation

$$p_t = p_0 (1 + \beta t)$$

where β has also been found by experiment † to be nearly $\frac{1}{273}$. This assumes that the *fundamental interval* is divided into 100 parts, so that we are using a centigrade scale. Thus, approximately,

$$p_t = p_0 \left(1 + \frac{t}{273} \right) = p_0 \frac{273 + t}{273}.$$

We now put $273 + t = T$ and $273 = T_0$, implying that the temperatures represented by T are measured from a new zero, 273° below the temperature of melting ice. ‡ With this notation

$$p_T = p_0 \frac{T}{T_0},$$

or $$\frac{p_T}{T} = \frac{p_0}{T_0},$$

* See Partington, *Text-Book of Inorganic Chemistry*, p. 147.

† The experimental values of α and β have been discussed on p. 137.

‡ Birge (1929) gives for the " ice-point ", T_0, the more accurate value
$$T_0 = 273·18 \pm 0·03° \text{ K.}$$
A more recent value is $T_0 = 273·16° \text{ K.}$

showing that, on this scale of temperature which agrees with the Kelvin scale, the pressure of the gas varies directly as the absolute temperature.

All the so-called " permanent " gases, such as hydrogen, oxygen, nitrogen, etc., conform approximately to this relation, which may be regarded as equivalent to the law of Charles.

In some investigations we shall use θ for temperature (in general) when no reference to the gas scale is implied.

Boyle's law is found by experiment to be obeyed with considerable accuracy by these " permanent " gases. When the temperature is kept constant, the volume of a given mass of gas varies inversely as the pressure. That is, at constant temperature, v varies inversely as p,

or $$pv = \text{constant}.$$

In the standard hydrogen thermometer the volume is kept constant, and, as we have seen,

$$p_T = \frac{p_0}{T_0} \times T.$$

But in this case $v_T = v_0$, hence

$$p_Tv_T = \frac{p_0v_0}{T_0} \times T,$$

or $$p_Tv_T = RT,$$

where R is a constant known as the gas constant.

The value of R is thus defined as $\dfrac{p_0v_0}{T_0}$.

It is worthy of special notice that R depends upon the mass of gas considered, and is in fact proportional to the mass, or, on the molecular theory, is proportional to the number of molecules dealt with (n say). The value of R/n, the gas constant for a single molecule, is known as Boltzmann's constant, k, and is of great importance in theoretical work. We have then $R/n = k$, or $R = nk$.

Experimental values. The values of some important constants connected with gases are collected in the following Table (46), which is based on the critical study of R. T. Birge (1929). Later results are given in Appendix I, p. 841.

In the equation $pv = RT$, the value of the gas constant R is directly proportional to the mass of gas considered For 1 gram-molecule (1 mole) the volume v_0 at normal temperature and pressure (N.T.P.) is 22414·1 cm.^{3}.

Certain standard conditions are here mentioned. The normal or standard temperature is in this case the ice-point, $0°$ C.

The normal or standard atmospheric pressure p_0 is defined in terms of the standard barometric height of 76 cm. of mercury, $p_0 = g\rho h$, where g is

In speaking of the density of a gas or vapour it is necessary to distinguish between the absolute and the relative density.

(1) The **normal density,** or simply the **density,** is the mass of unit volume measured under standard conditions of temperature and pressure. By chemists this is often expressed as the weight in grams of 1 litre (or 1000·027 c.c.) of the gas, or vapour, measured at a temperature of 0° C. under standard pressure defined as that due to 76 cm. of mercury.

(2) The **relative density** is the weight of any volume of the substance divided by the weight of an equal volume of pure hydrogen, measured and weighed under the same conditions. Densities are often given relative to that of oxygen (O = 16) at 0° C. and a pressure of 76 cm. of mercury.

As the pressure becomes smaller, the deviations from Boyle's law become less and less, and may be regarded as negligible at very small pressures. It may be assumed that, as the pressure tends to zero, the ratio of the *limiting densities* * ($p \to 0$) gives the exact ratio of the molecular weights (D. Berthelot, 1899).

Gas scale of temperature. As we have shown on page 48, it is possible to construct a gas thermometer which can be used at constant pressure, and in such a case the temperature t measured from the ice-point is *defined* by the equation $$v_t = v_0(1 + \alpha t)$$ where α has been found by experiment to be 0·003665 or approximately $\frac{1}{273}$.

Such a thermometer is not entirely suitable for use as a standard, and for many years the practical *standard* scale was that of the constant volume hydrogen thermometer. On this scale the temperature t, measured from the ice-point as zero, is *defined* by the equation $$p_t = p_0 (1 + \beta t)$$ where β has also been found by experiment † to be nearly $\frac{1}{273}$. This assumes that the *fundamental interval* is divided into 100 parts, so that we are using a centigrade scale. Thus, approximately,

$$p_t = p_0\left(1 + \frac{t}{273}\right) = p_0\frac{273 + t}{273}.$$

We now put $273 + t = T$ and $273 = T_0$, implying that the temperatures represented by T are measured from a new zero, 273° below the temperature of melting ice. ‡ With this notation

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or $\qquad p_T v_T = RT,$

where R is a constant known as the gas constant.

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The normal or standard atmospheric pressure p_0 is defined in terms of the standard barometric height of 76 cm. of mercury, $p_0 = g\rho h$, where g is

the (normal) acceleration due to gravity and ρ is the density of mercury. This gives as the value of p_0 or A_n, 1,013,249 dynes per square centimetre.

The gas constant for the mole, $R_M = \dfrac{p_0 v_0}{T_0}$, can now be calculated and is found to be 8·3136 joules per degree. It may also be expressed as 1·9864 cal.$_{15}$ deg.$^{-1}$ mole^{-1}.

As the number of molecules in 1 mole is $6·064 \times 10^{23}$ (N_0, Avogadro's number) the value of Boltzmann's constant (R_M/N_0) is

$$k = 1·3708 \times 10^{-16} \text{ erg deg.}^{-1}.$$

TABLE 46
SOME IMPORTANT CONSTANTS (BIRGE)

Acceleration of gravity (normal) -	$g = 980·665$ cm. sec.$^{-2}$.
Density of mercury at 0° C. - -	$\rho_0 = 13·59509$ gm. cm.$^{-3}$.
Normal atmosphere - -	$A_n = 1·013249 \times 10^6$ dyne cm.$^{-2}$.
Volume of perfect gas (0° C., A_n) -	$v_0 = 22·4141 \times 10^3$ cm.^{3} mole^{-1}.
Ice-point - - - -	$T_0 = 273·18°$ K.
Gas constant per mole - -	$R_M = 8·3136 \times 10^7$ erg deg.$^{-1}$ mole^{-1}.
Avogadro's number - -	$N_0 = 6·064 \times 10^{23}$ mole^{-1}.
Boltzmann's constant ($k = R_M/N_0$) -	$k = 1·3708_9 \times 10^{-16}$ erg deg. [1]

The ideal or perfect gas. We know that actual gases do not exactly obey Boyle's law at all temperatures, and do not all show the same increase in pressure for a given rise of temperature when the volume is kept constant.

In theoretical discussions it is convenient to imagine a gas which obeys with absolute accuracy laws which are only approximately true for real gases. This ideal gas is called a **perfect gas**. For an exact definition of the perfect gas two relations are required. The first condition is that the gas should obey Boyle's law accurately at any temperature whatever. The second condition is not so simple and will be more readily understood after we have studied the internal energy of the gas. The discussion of this relation will, therefore, be postponed for the present.

It may be said that hydrogen comes very near to the definition of a perfect gas. This gas is used in the standard thermometer chosen in defining the gas scale of temperature.

On the other hand, oxygen has been adopted by chemists as a standard in dealing with atomic weight determinations, its atomic weight being 16·000 by definition, and this gas has generally been used in determining the volume occupied by one gram-molecule of gas under standard conditions.

Non-perfect gases. We know that for a perfect gas the pressure p varies inversely with the volume v, provided that the temperature is constant. This is Boyle's law and it may be written in the form

$$pv = A.$$

We also know that the constant $A = RT$, where R is the gas constant and T is the absolute temperature.

Kamerlingh Onnes * modified this equation so that it would represent the behaviour of a real gas (see pp. 272 and 343), and utilised an expression of the form

$$pv = A + Bp + Cp^2 + Dp^3 + \dots,$$

where A, B, C ... are characteristic of each gas and vary with the temperature. Mathematically they are known as **virial coefficients.**

The coefficient A is again equal to RT, or if we assume v to be the volume of one gram-molecule, $A = R_M T$. The coefficients B, C, D, ... decrease in magnitude respectively. The term in B is therefore the most important : at low temperatures B possesses a large negative value, but becomes positive as the temperature rises. The temperature at which B becomes zero is called the **Boyle temperature,** because since the coefficients C, D, ... are all small compared with B the terms involving them only become important at high pressures, and consequently at this temperature the gas obeys Boyle's law with considerable accuracy over a wide range of pressure.

COMPRESSION AND RAREFACTION OF GASES

In his book entitled *An Experimental Inquiry into the Nature and Propagation of Heat*, published in 1804, John Leslie gives instructions for performing the following experiment (p. 533) :

" Having therefore fixed a delicate thermometer in the centre of a large receiver, extract most of the air, leaving perhaps only the tenth or hundredth part, and allow the apparatus to acquire exactly the temperature of the room. Then suddenly admit the air into the partial void, and the heat now disengaged will proportionally raise the general temperature."

The same effect could be observed " with some other species of gas ", the fact being mentioned that, on the admission of " hydrogenous " gas, " it suffered exactly the same change of temperature as atmospheric air ".

It is now a matter of common observation that when air is compressed by a pump—as in pumping up a pneumatic tyre—the temperature is raised, and it is not difficult to show that the temperature of air is decreased by rarefaction. Dalton was the first to measure such changes of temperature with any degree of accuracy.

Other investigators at the beginning of the nineteenth century made experiments on the compression and rarefaction of gases, including Gay-Lussac, whose work will be described later.

It would seem that Carnot was familiar with the fact that when a gas is compressed heat is evolved. It appears from his note-books that before his death (1832) he " had not only embraced the dynamical theory

* Kamerlingh Onnes, *Leiden Commun.*, No. 71 (1901).

of heat, but had planned many of those very experiments by which Joule subsequently established the equivalence of heat and work. He also gave an estimation of this equivalent [370 gram-metres or 3·63 joules per calorie], probably deduced from the same data as those employed by Mayer " (Preston).

Séguin (1839) examined the behaviour of steam in a steam engine and, assuming that the work given out in its expansion is the equivalent of the heat lost, obtained the value 369 gram-metres or 3·62 joules per calorie for the mechanical equivalent of heat.

Mayer (1842) discussed the heat developed by the compression of a gas, and assuming this to be the equivalent of the work expended in compression, he found 367 gram-metres or 3·60 joules per calorie as the value of the mechanical equivalent. In a later paper, published after Joule's experiments on gases were completed, Mayer referred to the earlier work of Gay-Lussac in support of his argument.

Joule on the compression and rarefaction of gases. In 1845 Joule published an important paper on the changes of temperature produced by the rarefaction and condensation of air. He made experiments to determine the absolute quantity of heat developed when air is compressed, and also the heat absorbed when air expanded. In each case he noticed that the quantity of heat represented the equivalent of the work spent or done. In the experiments on the compression of air, he found for the mechanical equivalent of the British thermal unit 823 and 795 foot-pounds, and in the experiments on expansion 820, 814 and 760 foot-pounds, in agreement with his earlier determinations.* In these experiments *external* work was done either on or by the gas.

This raises the important question of the *internal* energy of a gas, a matter which was for the first time satisfactorily investigated by Joule.

Gay-Lussac's experiment and Joule's repetition. In 1807 an important experiment was carried out by Gay-Lussac. He used two globes each of capacity 12 litres and each containing a sensitive thermometer (Fig. 215). Globe (1) contained air or some other gas (carbon dioxide or oxygen) at atmospheric pressure; globe (2) was exhausted.
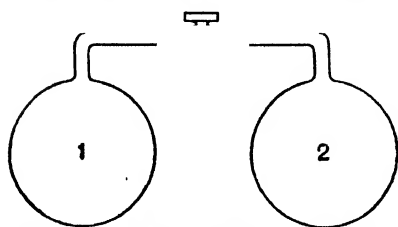
FIG. 215. GAY-LUSSAC'S APPARATUS

When the stopcock in the connecting tube was opened, the reading of the thermometer in the first globe fell a small amount, 0·61°. The reading of the thermometer in the

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* The corresponding values of J in joules per calorie are 4·43 and 4·25 in the compression experiments ; 4·38, 4·35 and 4·06 in the expansion experiments.

second globe rose by almost the same amount, 0·58°. Although the observed change is small, this may be taken to indicate that the first globe loses as much heat as the other gains. The correct explanation of the results was first given by Joule.

More accurate experiments on the same principle were carried out by Joule in 1845 to determine whether the temperature of a gas changed when an increase in volume occurred but no external work was done.

The apparatus used is shown in Fig. 216. In the primary experiment (Fig. 216 (a)), two copper vessels A and B were connected by a pipe

(a)   (b)
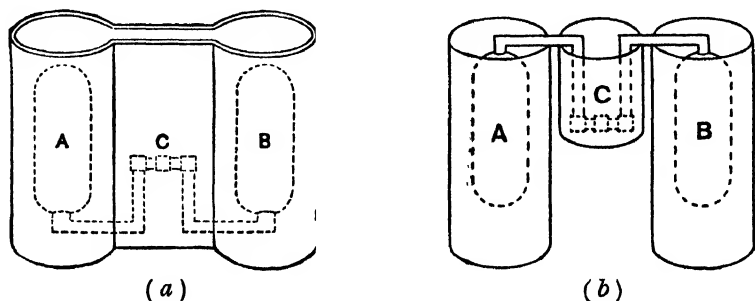
FIG. 216. JOULE'S APPARATUS

fitted with a carefully designed stopcock. The receiver A was filled with dry air at a pressure of 22 atmospheres; the second receiver was exhausted by means of an air pump. The vessels were placed in a water bath which served as a calorimeter. At the beginning of the experiment, after the bath had been stirred, the temperature was read by means of a delicate thermometer reading to $\frac{1}{200}$° F. The stopcock was opened and the air rushed from A into B so that the pressure in the two receivers was equalised. The water was again stirred and the final temperature found to be the same as the initial temperature. According to Joule this experiment proves that " no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power."

To analyse the experiment, the apparatus was inverted as in Fig. 216 (b). The vessels A and B were placed in separate baths, and a small bath was provided for the connecting pipe and the stopcock. When the stopcock was opened the temperature in the bath containing A fell, whilst the temperature in the two baths containing B and C rose. The heat lost by A is compensated by the heat gained by B and C. The gas in A does work in pushing forward gas in front of it into the empty vessel. In the vessels C and B work is done by the inflowing gas *on* the gas which has already entered.

In 1848 Joule summed up the conclusion based on experiments on air as follows : " the experiments, showing that the thermal effects of the condensation and rarefaction of air are the equivalents of the mechanical force [energy] expended in the one case and gained in the other, prove that the heat of elastic fluids consists simply in the *vis viva* [kinetic energy] of their particles." The words here interpolated represent the modern equivalent of the terms employed by Joule.

The experimental results are embodied in Joule's law for gases, which may be stated thus : When a gas expands without doing external work and without taking in or giving out heat (that is, without changing its internal energy) the temperature of the gas does not change.

Hence the internal energy of a perfect gas is a function of its temperature only. This statement is to be regarded as accurate for a perfect gas ; for actual gases it is true only to a first approximation, as was shown later in the more accurate porous plug experiments of Kelvin and Joule carried out between 1852 and 1862. These experiments have already been described in Chapter XVII, but they will be discussed further from the thermodynamic point of view at a later stage (p. 686).

From the standpoint of the molecular theory of gases, Joule's results imply that in the ideal gas the molecules are so far apart that any effect arising from cohesion between the molecules may be neglected, and even when encounters take place between molecules the process may be regarded as collision between perfectly elastic molecules.

In an actual gas attractive forces do exist between individual molecules, and in consequence the molecules possess potential energy. Expansion of the gas is accompanied by an increase in this potential energy because the average distance between the molecules is increased. Assuming that no external work is done and no heat is supplied from outside, this increase in potential energy can only take place at the expense of the kinetic energy. But this diminution in kinetic energy means a fall in the temperature of the gas.

However, in actual gases there is another and distinct effect arising from the same cause as deviations from Boyle's law, and this *may* be so large in comparison as to produce a rise instead of a fall in temperature.

Joule's law for a perfect gas. Let us now consider how this characteristic property of an ideal gas can be expressed mathematically from the standpoint of the first law of thermodynamics.

We have seen that for any system $Q - A$ is equal to $U_2 - U_1$. In Joule's first experiment (Fig. 216 (*a*)) there is no heat change ($Q = 0$), and no external work done ($A = 0$). We conclude that $U_2 = U_1$, that is, the internal energy of the gas is unchanged, and that therefore no internal work is done by an ideal gas during expansion.

In other words, the intrinsic energy of a perfect gas is independent of the volume which it occupies, the temperature θ being constant. Mathematically this means that

$$\left(\frac{\partial U}{\partial v}\right)_\theta = 0.$$

This relation is sometimes called Joule's law for a perfect gas.

SPECIFIC HEATS OF A PERFECT GAS

Difference between the specific heats C_p and C_v of a perfect gas. Let one gram-molecule (1 mole) of a perfect gas be enclosed in a cylinder, having cross-section of unit area, by means of a well-fitting piston. Let an amount of heat dQ be communicated to the gas and the resulting rise of temperature be dT. The equation $dQ = dU + dA$ must hold.

There are two important cases which are illustrated on the indicator diagrams in Fig. 217.
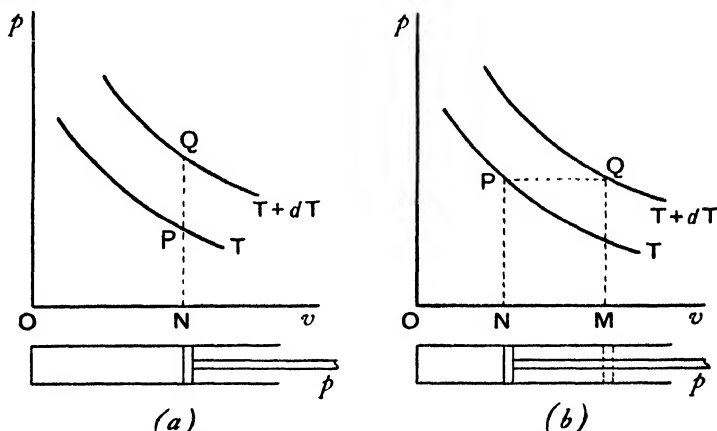
FIG. 217. DIFFERENCE BETWEEN THE SPECIFIC HEATS, C_p AND C_v, OF A PERFECT GAS

Case a. Volume maintained constant.

When the volume is constant no external work is done and the heat supplied serves to raise the temperature, and at the same time to increase the internal energy of the gas.

Then
$$dQ_v = dU,$$
or
$$C_v dT = dU.$$

Case b. Pressure maintained constant.

When the pressure is constant external work is done of amount

$$dA = p\,dx = p\,dv \text{ since the cross-section is unity.}$$

Hence
$$dQ_p = dU + p\,dv,$$
or
$$C_p dT = dU + p\,dv.$$

As the gas is assumed perfect, and its molecules do not exert any attraction upon one another, the change in the internal energy is the same in cases a and b.

Hence, on subtraction, $C_p dT - C_v dT = p\, dv$. But, for 1 mole of a perfect gas, using the gas scale of temperature,

$$pv = R_M T, \quad p(v + dv) = R_M(T + dT),$$

so that
$$p\, dv = R_M\, dT.$$

Hence
$$C_p dT - C_v dT = R_M\, dT,$$

or
$$C_p - C_v = R_M.$$

The equation expresses the fact that for a perfect gas the specific heat at constant pressure is greater than the specific heat at constant volume, and the difference between these two specific heats is equal to the gas constant.

This assumes that C_p, C_v and R_M are all expressed in the same units. If, however, C_p and C_v are in thermal units and R_M is in mechanical units the equation must be written

$$J(C_p - C_v) = R_M.$$

Mayer's method of calculating the mechanical equivalent of heat. The above result was actually employed in 1842 by Mayer in a calculation of the value of the mechanical equivalent of heat. The values of the specific heats in thermal units being known, and also the value of R in mechanical units, we can deduce the value of the mechanical equivalent of heat.

In his first experiment Mayer tacitly assumed that no internal work was done in the expansion of a gas. In a second paper, published in 1845, he referred to the experiment of Gay-Lussac in support of this assumption.

NUMERICAL VALUES FOR J BY MAYER'S METHOD. Although the method is strictly applicable only to ideal gases, it is of interest to consider the figures for air (Partington). In this case for 1 gm. of air $C_p = 0.2389$ cal. But, for air, Partington found $C_p/C_v = 1.403$, so that $C_v = 0.1702$ cal. and $C_p - C_v = 0.0687$ cal.

Let us assume that this difference is spent entirely in doing work against atmospheric pressure. The work done is the product of the pressure (1.0132×10^6 dynes) and the increase in volume 2.83 c.c. This latter figure is found approximately by taking $1/273$ of the volume (773.4 c.c.) of 1 gm. of air at $0°$ C. This gives for the work done

$$1.0132 \times 10^6 \times 2.83 \text{ ergs} = 2.867 \times 10^6 \text{ ergs}.$$

Hence $\quad J = \dfrac{2 \cdot 867 \times 10^6 \text{ ergs}}{0 \cdot 0687 \text{ cal.}} = 4 \cdot 174 \times 10^7$ ergs per calorie.

This corresponds to about 42,600 gm. cm. per calorie as compared with 36,500 gm. cm. per calorie found by Mayer (1842).

Generalisation of the expression for the difference in the two specific heats. * We have seen that for 1 mole of a perfect gas we may write

$$C_p - C_v = R_M.$$

For *any* unit mass (say 1 gm.) of gas, we have

$$c_p - c_v = R.$$

We shall now consider the more general expression which may be applied to *any* working substance the state of which may be defined by variables p, v and θ. We use θ here for temperature, as the results are quite general.

We start from the fundamental equation for internal energy

$$Q - A = U_2 - U_1,$$

which for an infinitesimal change may be written

$$dQ = dU + dA.$$

When we are dealing with *unit mass* of a substance the internal energy may be denoted u instead of U, and the equation may be written

$$dQ = du + dA.$$

This is the mathematical statement of the first law of thermodynamics. The external work dA may be taken equal to $p\,dv$.

Therefore $\qquad\qquad dQ = du + p\,dv.$

We may choose v and θ as the independent variables for representing the state of the substance.

The increase of the internal energy of unit mass, du, may then be expressed as a function of v and θ. There is a well-known mathematical expression in terms of partial differential coefficients according to which we may write

$$du = \left(\frac{\partial u}{\partial \theta}\right)_v d\theta + \left(\frac{\partial u}{\partial v}\right)_\theta dv.$$

Substituting this value in the expression above,

$$dQ = \left(\frac{\partial u}{\partial \theta}\right)_v d\theta + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right] dv.$$

Now considering the particular case in which the volume is kept constant ($dv = 0$), we get

$$dQ = \left(\frac{\partial u}{\partial \theta}\right)_v d\theta.$$

* This section may be omitted on first reading.

The specific heat at constant volume was defined as the ratio of the amount of heat to the change in temperature, that is,

$$c_v = \left(\frac{\partial Q}{\partial \theta}\right)_v ; \quad \therefore \quad c_v = \left(\frac{\partial u}{\partial \theta}\right)_v .$$

Consequently the specific heat at constant volume c_v is the rate of change of the internal energy with temperature when the volume is constant. Substituting that value in the general equation, we write the result as

$$dQ = c_v d\theta + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right] dv ;$$

$$\therefore \quad \frac{dQ}{d\theta} = c_v + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right] \frac{dv}{d\theta} .$$

This is a general equation for the specific heat $\frac{dQ}{d\theta}$ of a substance, and we see from it that the specific heat may assume all possible values according to the value of $\frac{dv}{d\theta}$. When the pressure is kept constant we find the value of c_p, the specific heat at constant pressure :

$$c_p = c_v + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right] \left(\frac{\partial v}{\partial \theta}\right)_p .$$

This equation determines the difference between c_p and c_v,

$$c_p - c_v = \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right] \left(\frac{\partial v}{\partial \theta}\right)_p ,$$

an equation which is true for a substance in any state.

Corollary. Let us apply our result to the particular case of an ideal gas, for which, putting T for θ, the gas equation $pv = RT$ holds. To define an ideal gas completely we make use of Joule's law, which tells us that the internal energy of a *perfect* gas is unchanged when the gas expands at constant temperature. In mathematical language this means that $\left(\frac{\partial u}{\partial v}\right)_\theta = 0$ (Joule's law for a perfect gas).

It follows that for an ideal gas

$$c_p - c_v = p \left(\frac{\partial v}{\partial T}\right)_p = R,$$

as is seen by differentiating $pv = RT$ with regard to T, keeping p constant.

For an actual gas $\left(\frac{\partial u}{\partial v}\right)_\theta$ is not exactly zero, but it is small in comparison with p. This means that for an actual gas the equation $c_p - c_v = R$ requires a small correcting term. For a liquid or a solid $\left(\frac{\partial u}{\partial v}\right)_\theta$ will be large in comparison with p.

Adiabatic transformations for a perfect gas. An adiabatic transformation is a change in which no heat is allowed to escape from the substance

or to enter it from any external source.   In an infinitesimal change of this kind dQ must be zero.   But as we have seen

$$dQ = du + dA$$
$$= du + p\,dv$$
$$= \left(\frac{\partial u}{\partial \theta}\right)_v d\theta + \left(\frac{\partial u}{\partial v}\right)_\theta dv + p\,dv$$
$$= c_v d\theta + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right]dv.$$

Hence for an adiabatic change in *any* substance

$$0 = c_v d\theta + \left[\left(\frac{\partial u}{\partial v}\right)_\theta + p\right]dv.$$

We now consider the particular case of the ideal gas for which, as we have seen, $pv = RT$ and $\left(\frac{\partial u}{\partial v}\right)_\theta = 0$.

Putting $\theta = T$, the condition for an adiabatic change of the perfect gas may be written

$$c_v dT + p\,dv = 0.$$

Let us now eliminate T by means of the gas equation so as to obtain a relation between p and v.

Differentiating the equation $pv = RT$ with respect to T, we have

$$p\,dv + v\,dp = R\,dT.$$

Substituting this value of dT in the previous equation, we get

$$c_v(p\,dv + v\,dp) + Rp\,dv = 0.$$

But we have proved that for a perfect gas $R = c_p - c_v$.

Hence

$$c_v v\,dp + c_p p\,dv = 0.$$

We wish to calculate the *ratio* of the two specific heats and we denote this ratio c_p/c_v by γ.   Consequently

$$\frac{dp}{p} + \gamma\frac{dv}{v} = 0,$$

and on integration this yields

$$\log p + \gamma \log v = \text{constant},$$

or

$$pv^\gamma = \text{constant}.$$

This is the condition which must be satisfied for the adiabatic change of a perfect gas.   Thus we obtain the very important result that for a perfect gas the equation of an adiabatic is $pv^\gamma = \text{constant}$.

It should be remarked that in carrying out the integration we have tacitly assumed that c_v, and therefore also c_p and γ are independent of

the temperature. This constancy is not implied in the definition of a perfect gas.

As we have already seen in Chapter XVI, there are other equations which may be deduced from this. Combining our equation with the equation $pv = RT$, it is easy to show that we get $Tv^{\gamma-1} = $ constant, and also $p = $ constant $\times T^{\frac{\gamma}{\gamma-1}}$.

Some numerical values. The work done in expansion through 1 c.c. under a *constant* pressure of p_0 1 atmosphere is called a c.c. atmosphere (c.c. atm.).

Since 1 atmosphere pressure = 1,013,200 dynes per sq. cm., this amount of work = 1,013,200 ergs = 0·02423 calories.

In the same way the work done in expansion through 1 litre under a constant pressure of 1 atmosphere is called a litre atmosphere.

This is 1000 times as great as the c.c. atm. and = 24·23 calories.

The volume v_0 of 1 mole of a perfect gas at N.T.P. is 22,414 c.c. If the expansion under a *constant* pressure of 1 atmosphere has this value, the work done = 0·02423 × 22414 calories.

For a perfect gas the relation $pv = RT$ holds good. Consequently the product p_0v_0 which we have just been considering can be represented as RT_0 provided R is expressed in suitable units.

Hence $$R_M = \frac{0 \cdot 02423 \times 22414}{273 \cdot 16} = 1 \cdot 988 \text{ calories per mole per } °C.$$

SPECIFIC HEATS OF REAL GASES

A table giving experimental values of C_p and γ for various gases has been given (p. 355) in Part I.

For monatomic gases like helium, argon and krypton the value of γ is very nearly $1\frac{2}{3}$ or 1·667. For diatomic gases such as oxygen, hydrogen, nitrogen, the value approximates to 1·4. For gases having more complex molecules the value of γ is smaller but is always greater than unity.

The kinetic molecular theory of gases throws some light on the values observed in the simpler cases. According to the principle of **equipartition of energy,** developed by Maxwell, Gibbs and Boltzmann, the energy of a body is equally distributed between the various degrees of freedom. For instance in an ideal monatomic gas the molecules are assumed to possess only kinetic energy of translation and no potential energy.

They have three degrees of freedom corresponding to the three directions of translational motion in space of three dimensions. The *mean* kinetic energy of a molecule, as given by the kinetic theory, is $\frac{3}{2}kT$, where k is Boltzmann's constant and T is the absolute temperature. The *mean* kinetic energy is therefore $\frac{1}{2}kT$ for each degree of freedom, and this value may be employed whether we are dealing with translation or rotation.

In dealing with a simple vibration half the energy is kinetic and half potential, so that the total is kT for a single vibrator.

For one mole of an ideal monatomic gas the internal energy U is entirely kinetic energy.

$$U = N\mathbf{w} = \tfrac{3}{2}NkT = \tfrac{3}{2}R_M T,$$

where $R_M \simeq 1\cdot988$ cal. per mole per °C.

The specific heat at constant volume is given by

$$C_v = \frac{dU}{dT} = \tfrac{3}{2}R_M,$$

and is approximately 2·982 cal. per mole per °C.

Since $C_p - C_v = R_M$, the specific heat at constant pressure is

$$C_p = \tfrac{3}{2}R_M + R_M = \tfrac{5}{2}R_M,$$

and is approximately 4·970 cal. per mole per °C.

For such an ideal gas $\gamma = C_p / C_v = \tfrac{5}{3} = 1\tfrac{2}{3} \simeq 1\cdot667$.

The experimental values for the inert gases and for mercury vapour are in satisfactory agreement with this value.

It is tempting to try to explain the fact that the value of γ for diatomic gases is about $1\tfrac{2}{5}$ by using a dumb-bell shaped molecule and postulating five degrees of freedom.* No entirely satisfactory explanation can be given of the observed values of the specific heats of a gas, or the values of γ, in terms of the classical system of dynamics. But by employing quantum-dynamics it is possible to explain the results both for the gaseous and for the solid state of matter.

WORKED EXAMPLE

Calculate the change of temperature of helium initially at 15° C., when it is suddenly expanded to 8 times its bulk. [*Ratio of specific heats = 5/3.*]

(L.U., B.Sc.)

If we assume that helium is a perfect gas and that the expansion is adiabatic, we may use the relation $Tv^{\gamma-1} = $ const.

In this case, assuming that the ice-point is 273° K.,

$T_1 = 288°$ K., $T_2 = $ final temperature, $v_2 = 8v_1$,   and $\gamma = 5/3 = 1\cdot667$;

$$\therefore \ 288 \times (v_1)^{0\cdot667} = T_2 \times (8v_1)^{0\cdot667};$$

$$\therefore \ T_2 = 288 \times (0\cdot125)^{0\cdot667}$$

$$= 288 \times 0\cdot2498$$

$$= 72° \text{ K., or } -201° \text{ C.}$$

Hence the temperature falls through 216° C.

* Jeans, *Dynamical Theory of Gases*, p. 192.

QUESTIONS

Chapter XXVII

1. Establish the relation $pv^\gamma = $ constant for a gas expanding adiabatically.

A mass of dry air at $15°$ C. is expanded adiabatically to double its volume. Calculate approximately its new temperature.   (E.U., Inter. Hons.)

2. Find an expression connecting the pressure and the volume of a mass of ideal gas during a reversible adiabatic change.

A gram of air at $275°$ C expands adiabatically to five times its initial volume Find the work done in its expansion, assuming that the air behaves as an ideal gas.

[Ratio of the specific heats of air $= 1.40$.   Gas constant for 1 gm. of air $= 2.88 \times 10^6$ ergs per degree C.]   (L.U., B Sc)

3. Find an expression for the work done when a quantity of air expands adiabatically from volume v_1 to volume v_2.

Calculate the work done in ergs, if $\gamma = 1.41$, the initial pressure being 76 cm. of mercury, the initial volume 1.5 litres and the final volume 6.0 litres.

4. Derive an expression for the work done in an isothermal expansion of a perfect gas.

Calculate the work done in compressing isothermally a litre of air at standard temperature and pressure to one-tenth of its initial volume.   (St. A. U.)

5. Find an expression for the difference between the two principal specific heats of a perfect gas.

For oxygen, the specific heat at constant pressure is 0.2175 and the density at N.T.P. is 0.001429 gm per c.c. Assuming $J = 4.191 \times 10^7$ ergs per calorie, find the specific heat of oxygen at constant volume and the ratio of the specific heats.   (E.U., M.A.)

6. Calculate the difference between the specific heats of oxygen, being given that a litre of oxygen at a temperature of $0°$ C. and under a pressure of 76 cm. of mercury weighs 1.429 gm.   Prove the formula you employ.   (St. A. U.)

7. The specific heat of nitrogen (molecular weight 28) at $0°$ C. is 0.235 at constant pressure and 0.175 at constant volume, the unit being cal. gm.$^{-1}$ deg.$^{-1}$. Comment on these results and explain how a value of Joule's equivalent could be obtained from them.

What other information would be needed?   (St. A. U.)

CHAPTER XXVIII

TRANSPORT PHENOMENA IN GASES

Reversible and irreversible processes. Before beginning the discussion of the Second Law of Thermodynamics it is desirable to point out an important distinction between two types of process in nature. In the last chapter we considered the change in volume of a gas contained in a cylinder fitted with a piston. Under suitable conditions this process is **reversible,** an expansion of the gas may be followed by a compression and the gas in this way restored to its original condition. But there are certain processes which are, in their nature, **irreversible.** For example, two different gases, when brought into contact, will diffuse into one another, as was observed by Priestley, who noticed that when the gases are once mixed they do not again separate. Dalton proved by a simple experiment that a lighter gas cannot rest upon a heavier one, the lighter gas passes downwards and the heavier gas upwards; or, in other words, the gases diffuse mutually into each other. According to Dalton, the diffusion of gases through each other is due to " that principle which is always energetic to produce the dilatation of the gas ".

Irreversible processes: viscosity, thermal conductivity and diffusion. In the treatment given in Chapter XIV we have observed that the encounters of the molecules of the gas are dynamically strictly reversible. It is, however, important to point out that the kinetic theory will enable us to explain certain irreversible processes such as viscosity, thermal conductivity and diffusion.

VISCOSITY. If a mass of gas at a uniform temperature is set in motion the mass may move as a whole, so that we have **mass-motion** of the gas. Or there may be **relative motion** between various portions of gas, one portion sliding with respect to another portion. If the gas is left to itself, such motion will rapidly become less, and in time will cease altogether. Thus we may say that the gas acts as medium possessing **viscosity.**

In an actual fluid composed of discrete molecules the molecular movements are extremely complicated, some molecules having a large and others a small velocity and these velocities are in various directions. But since the size of the molecules is very small and their number very great,

we may in imagination isolate a small volume of the fluid containing a very large number of molecules and treat the motion of this elementary volume as though it were the motion of a particle. The velocity of this element, or "particle of fluid", is strictly a statistical average and must be clearly distinguished from the velocity of a molecule.

When we seek to understand how the molecular theory accounts for viscosity, we may at first neglect the effect of cohesion between the individual molecules. Let us consider a stratum of gas between two

A ---------------------- B
E .... F
C ---------------------- D

FIG. 218. THEORY OF TRANS-
PORT PHENOMENA IN A GAS

horizontal planes AB and CD (Fig. 218). We suppose the plane CD to be fixed and the plane AB to be moving horizontally from left to right with some assigned velocity U. The gas in contact with this plane is assumed to be moving with the same velocity U. The gas in contact with CD is assumed to be at rest. The velocity of any intermediate layer EF is proportional to its distance from CD. The **velocity gradient** is found by dividing the velocity U by the distance between the planes AB and CD.

We fix our attention on a certain horizontal plane EF, which may be called the observational plane. The gas above this plane is moving faster than the gas below the plane, the faster moving gas tends to hurry on the slower moving gas, whilst at the same time the slower moving gas tends to retard the faster moving gas. Then there is set up a tangential stress, comprising both action and reaction, in the plane EF, and the corresponding force is called the force of viscosity. The kinetic theory of gases explains the existence of this tangential force as being due to the transference of molecules across the plane EF. We saw in Chapter XIV that the normal pressure of a gas on the walls of a containing vessel may be accounted for by considering the rate of change of momentum of the molecules bombarding a particular wall (say A in Fig. 219) of the vessel. In just the same way this tangential force may be accounted for by considering the rate of change of momentum due to molecules crossing the plane EF. Molecules moving downwards across EF possess, on the average, greater momentum in a horizontal direction than those moving upwards, so that the slower stream of gas is gaining momentum, and the faster stream is losing momentum. The gain of momentum implies force in the direction EF, and the loss of momentum implies force in the opposite direction. Thus viscosity may be regarded as **transference of momentum.**

THERMAL CONDUCTIVITY. In a similar way, if a mass of gas is at rest but is divided into two portions at different temperatures, after a time the interpenetration of the molecules between the two portions

will cause an equality of temperature throughout the whole mass. The gas acts as a medium possessing **thermal conductivity.** If we refer again to Fig. 218, we may regard the gas above the observational plane *EF* as being at a higher temperature than the gas below *EF*. Therefore molecules coming from *AB* and passing across *EF* will possess a greater kinetic energy than those coming from *CD*. In such a case the equalising of the temperature throughout the mass will be due to the **transference of kinetic energy.**

DIFFUSION. Again, if a vessel contains two different gases which exert no chemical action on each other, originally separated by the plane *EF* (Fig. 218), then after a sufficient time the molecules of each gas will penetrate into the space occupied by the other gas until they become uniformly mixed. Such a process is called **diffusion.** Molecules of the first gas will pass from *AB* across *EF*, and molecules of the second gas from *CD* will also pass across *EF* until uniformity is attained. In this case we see that such a phenomenon is due to the **transference of mass.**

MATHEMATICAL TREATMENT OF TRANSPORT PHENOMENA

So far we have been concerned with a merely qualitative description of these effects. It is possible to give an elementary mathematical treatment which is not without interest, but it must be stated clearly at the outset that the results so obtained will be only approximate. A more rigorous treatment shows that it is necessary to introduce various modifications in the numerical coefficients so as to deal with aspects of the phenomena which are here neglected.

We start with an approximate method of considering the motion of the molecules of a gas. It is due to Joule, and may be applied in our present problem. Joule thought of all the molecules contained in a cubic box (Fig. 219) as being divided into six streams moving parallel to the edges of the cube and therefore perpendicular to the six faces of the cube; for example, one stream of molecules may be thought of as moving from the face *A'* towards the face *A*, and a second stream as moving from *A* to *A'*, and similar streams in the case of the other pairs of faces. Let us fix our attention on the stream

FIG. 219. JOULE'S BOX

moving towards one face, say the face *A*, of the cube. This stream will have a mass equal to $\frac{1}{6}\rho$, where ρ is the density of the gas, assuming the cube to have unit volume. The total mass of gas moving towards the face *A* in one second will be $\frac{1}{6}\rho v$, where *v* is taken to represent the velocity of the stream of molecules. If we make the assumption that all the molecules in the stream have the *same* velocity *v*, we may identify *v* with
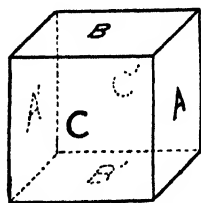
the root mean square velocity $\mathbf{C}$ (p. 318). For convenience we shall speak of v as the Joule velocity.

We shall now discuss these three phenomena of viscosity, thermal conductivity and diffusion quite generally. We shall treat the problem from the point of view of the transport of a certain magnitude within the gas itself, due to the movements of the individual molecules. The same type of mathematical reasoning can be applied to each case. As we have already seen above, viscosity may be regarded as transport of momentum, thermal conductivity as transport of kinetic energy, and diffusion as transport of mass.

It is desirable to notice that in all these transport phenomena we are no longer dealing with a *steady state* of the medium, as in the derivation of Boyle's law, but with a condition that *varies with time* in the sense that the magnitude concerned is transferred at a certain rate across unit area.

Let us picture a cloud of molecules moving in all directions, and suppose that *any* magnitude G is attached to each molecule, the value of G varying progressively from one region of the gas to another.

We take a plane EF (Fig. 220) which we may call the plane of observation, and we assume that the property of G has the same average value
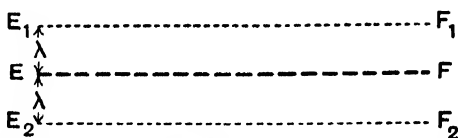
$$E_1 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots F_1$$
$$\lambda$$
$$E \;-\;-\;-\;-\;-\;-\;-\;-\;-\;-\;-\;-\; F$$
$$\lambda$$
$$E_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots F_2$$

FIG. 220.   TRANSPORT OF ANY MAGNITUDE G ACROSS AN OBSERVATION PLANE

at all points on this plane. Let us pass from EF to a neighbouring parallel plane E_1F_1 situated at a distance δz from EF. The value of the magnitude G changes to $G + \delta G$, and if we assume a linear law, we may write

$$\delta G = A \, \delta z, \text{ where } A \text{ is a constant.}$$

In the limit when $\delta z \rightarrow 0$, we may write $\dfrac{dG}{dz} = A$, where A is termed the **gradient of the magnitude** in the z-direction.

For simplicity, let us assume that the free path of any molecule is equal to the mean free path λ. We will consider the two planes E_1F_1 and E_2F_2 on either side of our observation plane EF, parallel to it, and situated at a distance λ from it (Fig. 220).

According to the simple theory of Joule already described, we may write the number of molecules crossing unit area of the surface EF in unit time in the direction z as equal to $\frac{1}{6}nv$, where n is the concentration or molecular density, and v is the Joule velocity for the gas.

The amount of the magnitude G carried across unit area of the observation plane EF in unit time from the plane E_1F_1 is given by

$$Q_1 = \tfrac{1}{6}nv \times \left(G + \lambda \frac{dG}{dz}\right).$$

Similarly, the amount from the plane E_2F_2 is given by

$$Q_2 = \tfrac{1}{6}nv \times \left(G - \lambda \frac{dG}{dz}\right);$$

$$\therefore\ Q = Q_1 - Q_2 = \tfrac{1}{3}nv\lambda \frac{dG}{dz}.$$

This is the total amount of the magnitude G carried across unit area of EF in unit time.

Let us apply this general equation to the three particular cases of viscosity, thermal conductivity and diffusion. The same method of treatment will be employed in each case.

1. **Viscosity.** Viscosity is transport of momentum; therefore we write $G = $ momentum parallel to $Ox = mu$ (say),

where m is the mass of a molecule, and u its component velocity in the direction Ox.

$$\therefore\ \frac{dG}{dz} = m\frac{du}{dz} = m \times (\text{velocity gradient});$$

$$\therefore\ Q = \tfrac{1}{3}nv\lambda m \times (\text{velocity gradient}).$$

According to Newton's laws of motion, the rate of change of momentum is equivalent to force, and hence, since we are considering unit area, this expression for Q measures the tangential stress.

The coefficient of viscosity (η) is defined as the ratio between the tangential stress and the velocity gradient.

$$\therefore\ \eta = \frac{\text{tangential stress}}{\text{velocity gradient}} = \frac{Q}{\text{velocity gradient}};$$

$$\therefore\ \eta = \tfrac{1}{3}nv\lambda m.$$

Finally, since the density of the gas (ρ) is given by $\rho = nm$, we may write

$$\eta = \tfrac{1}{3}\rho v\lambda.$$

2. **Thermal conductivity.** Thermal conductivity is transport of kinetic energy. This energy is in the form of heat. Let $c_v = $ specific heat of the gas at constant volume. This is the thermal equivalent of the increase in the total kinetic energy of 1 gm. of the gas due to unit rise in temperature. If unit mass of the gas contains n molecules, each of mass m, then the thermal equivalent of the total kinetic energy of a molecule at an absolute temperature T equals mc_vT, or

$$\mathbf{w} = mc_vT.$$

In this case we may assume for G the mean kinetic energy ($\mathbf{w}$) of a molecule at any point in the gas, so that $\mathbf{w}$ is a function of z.

$$\therefore \ \frac{dG}{dz} = \frac{d\mathbf{w}}{dz} = mc_v \frac{dT}{dz}.$$

$\dfrac{dT}{dz}$ is called the temperature gradient.

$$\therefore \ Q = \tfrac{1}{3} nv\lambda mc_v \times (\text{temperature gradient}).$$

Now Q is the total flow of energy across unit area of the plane in unit time, and this energy is in the form of heat.

The coefficient of thermal conductivity (K) of a gas is defined as the ratio between the quantity of heat transmitted across unit area in unit time and the temperature gradient.

$$\therefore \ K = \frac{Q}{\text{temperature gradient}} = \tfrac{1}{3} nmvc_v\lambda = \tfrac{1}{3} \rho vc_v\lambda,$$

where ρ is the density of the gas as before, and $\rho = nm$.

3. **Diffusion.** Diffusion is transport of mass. We will consider the simplest case, namely that of self-diffusion, when a gas diffuses into itself. The coefficient of self-diffusion (Δ) measures the rate at which selected molecules of a homogeneous gas diffuse into the remainder. Cotter * draws a simple analogy, and supposes that " the column consists of a single gas, the molecules in the upper half having been originally coloured red and those in the lower half blue ". We will consider the red molecules as they interpenetrate the boundary surface. If n is the molecular density (or number of molecules in unit volume) of both kinds of molecules, and n_1 and n_2 the molecular density of the red and blue molecules respectively, then $n = n_1 + n_2$. We may put G equal to the ratio of the number of red molecules to the sum of the numbers of the red and blue molecules in the stratum.

Then
$$G = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n},$$

$$\therefore \ \frac{dG}{dz} = \frac{1}{n} \frac{dn_1}{dz}.$$

This function is called the concentration gradient.

Thus we have $Q = \tfrac{1}{3} nv\lambda \times (\text{concentration gradient}).$

In this case Q is the number of molecules of the gas which cross unit area of the observation plane in unit time. That is to say, Q is the rate of diffusion of the gas.

* Preston, *Theory of Heat* (Fourth edition, 1929), pp. 814-15.

The coefficient of self-diffusion of a gas (Δ) is defined as the ratio between the rate of diffusion and the concentration gradient.

$$\therefore \; \Delta = \frac{Q}{\text{(concentration gradient)}} = \tfrac{1}{3}v\lambda.$$

We may note that strictly speaking the mass of one molecule (m) should be taken into account, because the phenomenon of diffusion is regarded as the transport of mass rather than as the number of molecules involved. But since the factor m would appear equally on both sides of the equation, it cancels out, and consequently has been omitted in order to simplify the calculation.

Relations between the coefficients. From the elementary theory given above, we can at once deduce simple equations connecting the three coefficients of viscosity η, thermal conductivity K, and self-diffusion Δ.

Conductivity and viscosity : $K = c_v\eta.$
Viscosity and diffusion   : $\eta = \Delta\rho.$
Conductivity and diffusion : $K = \Delta\rho c_v.$

These relations are not in accurate agreement with the numerical values obtained by experiment. This is due to the omission of the numerical coefficients already mentioned, which are demanded by a more rigorous treatment. They do, however, yield values of the correct order of magnitude.

MAXWELL'S LAW OF GASEOUS VISCOSITY

The results which we have obtained from theory indicate that both the viscosity and the thermal conductivity of a gas are independent of the density, for the mean free path (λ) is inversely proportional to the density (ρ), and consequently $\rho\lambda$ is constant. This conclusion is known as Maxwell's law of gaseous viscosity.* It was predicted by Maxwell on purely theoretical grounds. At first sight the result seems extremely improbable, but it has received striking experimental confirmation † and may be regarded as strong evidence in favour of the kinetic theory. Maxwell's law will not apply when the density of the gas is very small, because in a very rare gas the mean free path becomes comparable with the dimensions of the apparatus.

At very low pressures it is no longer permissible to treat the gas as a continuous medium. It is necessary to consider the molecular structure, and the rate of flow is limited by the collision frequency between mole-

* This must not be confused with Maxwell's law of distribution of molecular velocities to be discussed in Chapter XLII.

† It was shown by Boyle in 1660 that the oscillations of a pendulum die away just as rapidly in a rare gas as in a dense gas, thus providing in anticipation confirmation of Maxwell's law.

cules. At such low pressures " where the value of the mean free path is greater than the radius of the tube, the intermolecular collisions become less numerous than the collisions of the molecules with the containing walls ". Knudsen suggests the term **molecular flow** as applicable in such cases. Here the coefficient of viscosity loses all significance, and the flow is governed by the collisions with the wall of the tube.

NUMERICAL RESULTS BASED ON TRANSPORT PHENOMENA

We are now in a position to undertake various numerical calculations, which are of considerable importance. In making these calculations we shall assume that the Joule velocity v may be treated as equivalent to the root mean square velocity **C**.

1. **Mean free path.** The theory which we have already given shows that the coefficient of viscosity is given by the equation

$$\eta = \tfrac{1}{3}\rho v \lambda. \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

This provides us with a means for determining the mean free path, for, as we have already seen (p. 318), the fundamental expression for the pressure of a gas is given by

$$P = \tfrac{1}{3}\rho v^2. \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

Therefore between these two equations we may eliminate v. The first equation gives us $\lambda = \dfrac{3\eta}{\rho v}$, and the second equation gives us $\dfrac{1}{v} = \sqrt{\dfrac{\rho}{3P}}$.
Therefore

$$\lambda = \frac{3\eta}{\rho} \times \sqrt{\frac{\rho}{3P}} = \eta \sqrt{\frac{3}{P\rho}}.$$

As an example, consider the case of hydrogen at 0° C. The coefficient of viscosity η in C.G.S. units is approximately 0·00008. The standard atmospheric pressure P is 1014000 dynes per sq. cm., and under standard conditions the density ρ is very nearly 0·00009 gm. cm.$^{-3}$. Substituting these values, we find that the mean free path λ is equal to $1\cdot45 \times 10^{-5}$ cm.

2. **Collision frequency.** We may also deduce the value of the collision frequency, that is to say, the average number of collisions made per second by a molecule. This is equal to $\dfrac{\text{mean speed}}{\text{mean free path}}$, or $\dfrac{v}{\lambda}$. Dividing equation (2) by equation (1), $\dfrac{v}{\lambda} = \dfrac{P}{\eta}$. The numerical value for hydrogen is $1\cdot25 \times 10^{10}$ collisions per second.

3. **Molecular diameter.** We saw in Chapter XV (p. 335) that if the value of the mean free path of a molecule in a gas were known, then its diameter s could be determined by means of the relation $\lambda = \kappa \dfrac{1}{\pi s^2 n}$, where κ is a numerical coefficient. Since λ can be found from a knowledge of transport phenomena, we are now in a position to calculate s.

Let us take the case of hydrogen as an example. We have already found $\lambda = 1\cdot45 \times 10^{-5}$ cm. If we assume Maxwell's value of $0\cdot707$ for κ, and Millikan's value of $2\cdot705 \times 10^{19}$ for n, we may write

$$s = \sqrt{\frac{\kappa}{\pi n \lambda}} = \sqrt{\frac{0\cdot707}{\pi \times 2\cdot705 \times 10^{19} \times 1\cdot45 \times 10^{-5}}}$$

$$= 2\cdot37 \times 10^{-8} \text{ cm.}$$

The radius of the hydrogen molecule is one-half of this value, and is equal to $1\cdot18 \times 10^{-8}$ cm.

" The first numerical estimate of the diameter of a molecule was made in 1865 by Loschmidt from the mean path and the number of molecules. Independently of him and of each other, Johnstone Stoney (1866) and Sir William Thomson (1870) published results of a similar kind, those of Thomson being deduced not only in this way, but also from considerations derived from the thickness of soap bubbles, and from the electric action between zinc and copper."

Table 47 shows some values of the radius of molecules of different gases calculated by Jeans * by various methods. It will be observed that

TABLE 47

Molecular Radius ($\frac{1}{2}s$ in A.U.) Jeans

	Hydrogen	Nitrogen	Carbon dioxide	Helium
Diffusion - - - -	1·36	1·92	2·19	—
Viscosity - - - -	1·36	1·89	2·31	1·09
Thermal conductivity - -	1·36	1·89	2·42	1·10
Mean - - -	1·36	1·90	2·31	1·10
Deviations from Boyle's law -	1·27	1·78	1·71	0·99
Maximum density : upper limit for $\frac{1}{2}s$ - -	1·97	1·99	2·03	2·00
Dielectric constant : lower limit to $\frac{1}{2}s_\infty$ - -	0·92	1·21	1·41	0·60

Here $\frac{1}{2}s_\infty$ represents the value for very high temperatures.

the value for the radius of the hydrogen molecule is somewhat greater than that calculated above, because slightly different assumptions were made at the start. The values are, however, of the same same order of magnitude.

The first three estimates in the table are obtained from consideration

* *The Dynamical Theory of Gases*, Chapter XIV.

of transport phenomena and depend on the mean free path, in which case we are measuring the *cross-section* of the molecule.

In measuring the deviations from Boyle's law we are virtually measuring the *volume* of the molecule.

Another estimate for the molecular radius may be formed by considering the maximum density of the substance in the solid or liquid state. This gives us only an upper limit for the molecular radius. Jeans also gives other methods: for example, from a knowledge of the value of the dielectric constant. This gives a lower limit to the values of $\frac{1}{2}s$. We see then, from a study of the table, that the results obtained are consistent with one another, especially when we consider that helium is the only gas mentioned for which the molecule is composed of a single atom. We can obtain more definite knowledge as to the structure of the hydrogen molecule or the nitrogen molecule from a study of band spectra. It is found that such a molecule is shaped more like a dumbbell than a sphere, two massive particles (nuclei) being linked together by mutual attraction. Other molecules are still more complicated in shape, for example, in the molecule of ozone we have three atoms of oxygen linked together. We can scarcely expect that in such complicated molecules the results would agree exactly with those deduced on the assumption that the molecule is spherical.

WORKED EXAMPLE

Calculate the difference in the mean free path of helium at atmospheric pressure at $0°C.$ *and* $100°C.$ *[Viscosity of helium in C.G.S. units $= 0·00019$ at $0°C.$ and $0·00023$ at $100°C.$; Density of helium $= 0·0001785$ gm. per c.c. at $0°C.$]*

We employ the formula 　　　　$\lambda = \eta \sqrt{\dfrac{3}{P\rho}}.$

For one atmosphere, $P = 1,013,000$ dynes per c.c.

$$\therefore \ \lambda_0 = 0·00019 \sqrt{\frac{3}{1,013,000 \times 0·0001785}} = 3·97 \times 10^{-5} \text{ cm.}$$

To calculate λ_{100}, we must remember that $\rho_0 = \rho_{100}(1 + 100\alpha)$ where the coefficient of expansion of helium $\alpha = 0·00367$ per °C.

Hence, 　　　　$\rho_{100} = \dfrac{0·0001785}{1·367} = 0·0001296$ gm. per c.c.

and 　　　$\lambda_{100} = 0·00023 \sqrt{\dfrac{3}{1,013,000 \times 0·0001296}} = 5·26 \times 10^{-5}$ cm.

$$\therefore \ \lambda_{100} - \lambda_0 = 1·29 \times 10^{-5} \text{ cm., say } 1·3 \times 10^{-5} \text{ cm.}$$

QUESTIONS

Chapter XXVIII

1. Explain how the kinetic theory may be employed to deduce a relation between the thermal conductivity, viscosity and specific heat of a gas. Discuss the extent to which you would expect the deduction to agree with the facts.

(E.U., M.A. Hons.)

2. Describe the main features of the phenomena of diffusion in gases. State and explain with the help of the kinetic theory, the law which governs the rates at which gases diffuse through a partition containing exceedingly fine apertures. (L.U., B.Sc.)

3. Show that according to the kinetic theory, the conductivity of a gas for heat at different temperatures is proportional to its viscosity.

How has the variation of the viscosity of gases with temperature been determined experimentally? (St. A. U.)

4. Explain how the elementary kinetic theory accounts for the viscosity of a gas. Hence derive and discuss an expression for the coefficient of viscosity.

(L.U., B.Sc.)

5. Discuss Maxwell's law that the viscosity of a gas is independent of the density, and show how it affords evidence in favour of the truth of the kinetic theory. Explain why the law can no longer be regarded as valid at very low pressures.

CHAPTER XXIX

THE SECOND LAW OF THERMODYNAMICS

The work of Sadi Carnot. We begin consideration of this subject by examining the work of the brilliant French engineer Sadi Carnot, who set before himself the problem of determining *how* work is obtainable from heat in a heat engine. The second son of a mathematician and engineer, he was born in Luxemburg on June 1, 1796, and was taught mathematics by his father. In 1812 he gained admission to the École Polytechnique, and in 1814 passed into the Corps of Engineers at Metz. In 1828 he retired from the army, having reached the rank of captain of engineers. " He made himself familiar with mechanical engineering and various industries, and it was the absence of any exact theory of the steam engines of Newcomen, Watt, Smeaton, and Trevithick which led him to the study of heat and to writing his *Réflexions.*" This essay was printed in 1824 under the title *Réflexions sur la puissance motrice du feu et sur les moyens propres à la développer.* His work attracted little attention and might have been lost sight of altogether had it not been for a paper of Clapeyron (1834) which brought his original views to the notice of Lord Kelvin. Carnot's essay was reprinted in 1871 and again in 1878, with a letter from his younger brother Hippolyte (father of a President of the French Republic), a biographical sketch and extracts from his manuscripts. The essay was translated by R. H. Thurston in 1890 as *The Motive Power of Heat.* Sadi Carnot died in the cholera epidemic of Paris in 1832.

The term **motive power** used by Carnot is evidently equivalent to work or energy, as is clear from the following passage :

" We use the expression motive power (*puissance motrice*) to express the useful effect that a motor is capable of producing. This effect can always be regarded as the elevation of a weight to a certain height ; it is measured by the product of the weight and the height through which it is raised."

Carnot introduced two new conceptions, embodying principles of fundamental importance : (1) the cyclic process, (2) the idea of reversibility.

(1) By a **cyclic process** is meant a series of changes undergone by the working substance, in which process a certain amount of work is performed subject to the condition that the substance is brought back exactly to its initial condition.

(2) By the **reversibility** of the process is meant the possibility of reversing the changes in the series so that heat may be taken from the condenser and restored to the source by the expenditure of work.

Basing his argument on these conceptions and assuming the truth of the principle that perpetual motion is impossible, Carnot arrived at the conclusion that no engine can have a greater efficiency than a reversible engine. Another result based on the same assumptions was stated as follows :

" The maximum of motive power resulting from the employment of vapour is also the maximum motive power realisable by any means whatever."

This proposition was enunciated in more general form later in the essay after considering an ideal heat engine :

" The motive power of heat is independent of the agents set to work to produce it ; its quantity is fixed uniquely by the temperatures of the bodies between which the transport of heat takes place."

This statement presupposes that each of the methods employed in producing motive power reaches the perfection of which it is susceptible.

Sir Joseph Larmor in 1918 described the argument of Carnot as " perhaps the most original in physical science, whether as regards simple abstract power or in respect of grasp of essential practical principles."

It is to be remembered that in 1824 Carnot adhered to the caloric theory, but later became convinced of the truth of the dynamical theory of heat. It is possible to restate his argument in terms of the latter theory, and we shall now proceed to examine carefully the steps of the reasoning and to consider the statement and significance of the Second Law of Thermodynamics.

A cycle of operations. Any practical heat engine which is to work continuously must go through a succession of cyclic changes. Any series of operations by which the body or the working substance under consideration is finally brought to the same state in all respects as at first is called a **cycle of operations.** This important idea of a cyclic process was introduced by Carnot in his essay of 1824. He wrote : " If a body, having experienced a certain number of transformations, be brought identically to its primitive physical state as to density, temperature, and molecular constitution, it must contain the same quantity of heat as that

which it initially possessed." This fundamental principle of Carnot is, as Tait remarks, evidently axiomatic and is true whatever theory is adopted as to the nature of heat.

It is not enough to give a certain quantity of heat to a vapour, allow it to expand against a resistance and so do work, and then proceed to find the relation between the heat supplied and the work done. The vapour is left in a state different from that in which it started. The cycle must be completed, by bringing the working substance back to its old volume and temperature, before we can reason in a satisfactory way about any relation between the heat given to it and the work done. The changes taking place in the condition of the working substance and
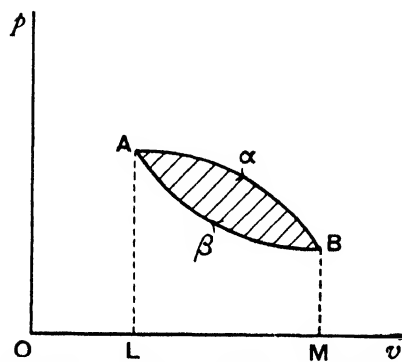
FIG. 221.   CYCLIC PROCESS SHOWN ON
      AN INDICATOR DIAGRAM

the work done in a cycle may easily be represented in an indicator diagram (Fig. 221), where the two coordinates are the pressure and the volume.

Starting from a certain state represented by the point A, we may suppose a change to a state B by a chosen path $A\alpha B$. Then we may suppose that the return from state B to state A takes place by some other path $B\beta A$. In the first change the work done by the substance as it expands is repre-
sented by the area $A\alpha BML$. In the second stage the work done on the substance as it contracts along the path $B\beta A$ is represented by the area $B\beta ALM$. The difference between these two quantities is the work done during the cycle and is represented by the difference between these areas, $A\alpha BML - B\beta ALM$, or the area $A\alpha B\beta A$, shown shaded in the diagram.

The substance is in the same state at the beginning and at the end of the cycle. Consequently the internal energy is unchanged. It follows that the heat taken in during the cycle is equal to the net amount of work done by the substance. Thus the area of the cycle represents both the work done and the heat taken in during the cycle.

The ideal heat engine. In ordinary phraseology when we speak of an " engine " we think of some mechanical arrangement containing pistons, connecting rods, wheels and so forth. In the theory of heat we are not concerned with the mechanical arrangements at all, but merely with the amount of heat supplied or given out, and with the amount of mechanical work done, though some of this mechanical work may be dissipated in the working parts of an actual engine.

Further, it is a matter of detail, and in nowise affects fundamental principles, whether steam, coal gas, or air be employed as the " working substance ", and we may generalise the reasoning by regarding the working substance as any substance in any way affected by heat. For the purpose of obtaining clear views of the action of an engine we consider the working of " an engine of a species entirely imaginary—one which it is impossible to construct, but very easy to understand " (Maxwell). Following Carnot we therefore picture an ideal heat engine as shown in Fig. 222.
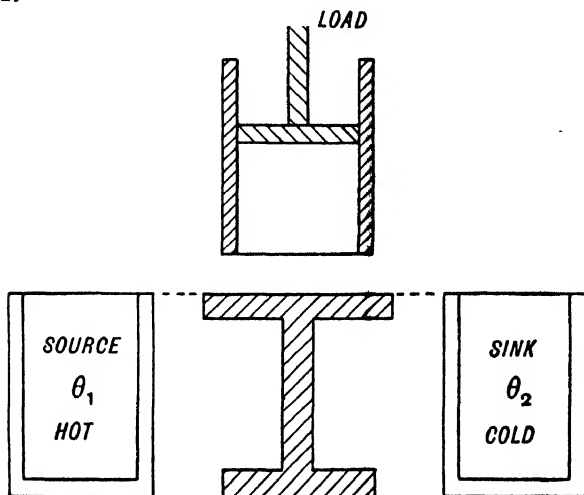
FIG. 222. IDEAL HEAT ENGINE (CARNOT)

The working substance is contained in a vertical cylinder constructed with non-conducting walls and provided with a non-conducting horizontal piston. The lower end of the cylinder is assumed to be perfectly conducting. We must have also a non-conducting table on which the cylinder may be placed ; a hot body to serve as a source of heat, maintained at a definite temperature θ_1 ; and a cold body to serve as a sink or condenser, maintained at a temperature θ_2. These two bodies which act as reservoirs of heat must be so large that their temperature remains practically unchanged during any transfer of heat to or from the cylinder. The cylinder may be placed on any one of these three stands and may be moved from one to the other without friction. A definite load may be applied to the piston by means of the piston rod, and the amount of the load may be varied at will so as to alter the volume of the working substance.

Carnot's cycle. The working substance is then supposed to go through a cycle of operations consisting of four stages. The trans-

formations may be represented in a geometrical form, as was shown by Clapeyron (1834), on the indicator diagram (Fig. 223). To start with we assume that the working substance is at the temperature θ_2 of the cold reservoir. On the indicator diagram the state is represented by the point A.
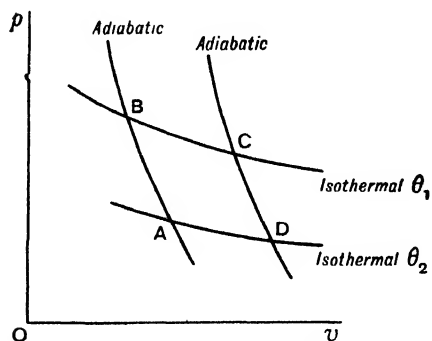
FIG. 223. CARNOT'S CYCLE

OPERATION 1. Place the cylinder on the non-conducting stand. No heat can enter or leave the cylinder, that is to say, any change taking place must be adiabatic. Compress the working substance by pushing in the piston. The temperature will rise above the temperature θ_2, and the process may be continued until the temperature becomes equal to that of the source θ_1. On the indicator diagram the change is represented by part of an adiabatic curve, the final condition being shown by the point B.

OPERATION 2. The cylinder is now removed from the non-conducting stand and placed on the source. The substance is allowed to expand isothermally, at the constant temperature θ_1. In the expansion, heat will be absorbed from the source, and we may suppose the process continued until some definite but arbitrary quantity of heat (Q_1) has been absorbed. This change is isothermal, and the condition of the working substance is represented as part of an isothermal curve, the final condition being shown on the diagram as C. In the change from B to C, Q_1 units of heat have been absorbed by the working substance from the hot reservoir.

OPERATION 3. The cylinder is again placed on the non-conducting stand and the working substance is allowed to expand adiabatically until the temperature falls to that of the sink. The curve CD representing this change is an adiabatic curve, and the temperature at D is θ_2.

OPERATION 4. The cylinder is placed on the sink and an isothermal change takes place at the temperature θ_2, the working substance being compressed until the point A is reached. DA is then an isothermal curve. In this last operation a certain amount of heat Q_2 is rejected to the sink.

The working substance has now returned to its initial condition, and the final state at A is the same as the initial state. The mechanical work done in the cycle is represented by the area $ABCD$, and it must be equal to $Q_1 - Q_2$, when all quantities are expressed in mechanical units.

We define the **efficiency** (ϵ) of the heat engine as the ratio of the work done to the heat taken in from the source, or, in symbols,

$$\epsilon = \frac{Q_1 - Q_2}{Q_1}.$$

Reversibility of the cycle. The other conception of great importance introduced by Carnot was that of reversibility. This means that each stage in the cyclic process can be carried out in the opposite sense. Carnot's cycle of operations just described is a reversible cycle. Starting from the point A, the working substance may expand at constant temperature till D is reached, heat of amount Q_2 being absorbed from the cold reservoir. This is Operation 4 reversed. Then an adiabatic compression may take place from D to C till the temperature is equal to that of the source. This is Operation 3 reversed. The substance may then be compressed from C to B, heat of amount Q_1 being rejected to the hot reservoir. This is Operation 2 reversed. Finally, the substance may expand from B to A adiabatically. This is Operation 1 reversed.

In this reversed cycle the amount of work spent is equal to $Q_1 - Q_2$. The quantity of heat Q_2 taken from the cold body is smaller than the quantity of heat Q_1 given to the hot body. The ideal engine now acts as a refrigerating machine, transferring heat from a body at a low temperature to a body at a higher temperature by the expenditure of mechanical work by some outside agency. We have previously suggested the term " heat pump " to describe such an arrangement.

It is, however, important to consider the reversibility of the individual operations in the cycle. This reversibility depends on the operations being carried out so slowly that at each stage the substance is virtually in thermal and mechanical equilibrium with its surroundings. This means that *the working substance is guided through a series of states which may be regarded as a succession of equilibrium positions.* For example, when the cylinder is in contact with the source, heat can only pass from the source to the cylinder, provided there is a temperature difference between source and cylinder ; but this difference is assumed to be infinitesimal, so that there is almost thermal equilibrium between source and cylinder. Similarly, when the cylinder is placed on the cold reservoir and is giving out heat, its temperature must be by an infinitesimal amount higher than that of the reservoir. Again, when the cylinder is placed on the non-conducting stand, the external pressure must exceed the internal pressure due to the working substance by an infinitesimal amount when the piston is moving inwards, and the converse must hold when the piston is moving outwards. But these pressure differences are so small that there is virtually mechanical equilibrium during the

operation. All the operations which we have been considering may be regarded, in the sense considered, as reversible operations. It is this fact which gives its importance to the reversible cycle of Carnot.

Reversible and irreversible transformations. The reversible processes or operations assumed in Carnot's reasoning are *ideal*. The actual operations of nature are commonly irreversible. It is just this difference which is emphasised in Carnot's argument and is embodied in the second law of thermodynamics. This law, which is concerned with the *direction* in which a process takes place in nature, we shall presently consider. According to Carnot, the test or condition for securing maximum efficiency under given circumstances is reversibility.

A reversible process in the thermodynamic sense is defined by Partington as " one which can be performed backwards, so that *all* changes occurring in any part of the direct process are *exactly* reversed in the corresponding part of the reversed process, and no other changes are left in external bodies ".

On the indicator diagram (Fig. 224), we may take two points A and B representing two states. A certain path from A to B corresponds to

FIG. 224. REVERSIBLE CHANGE
SHOWN ON AN INDICATOR DIAGRAM

some process by which the state is changed. When this process is reversible, any small element PQ represents a change which can be carried out either from P to Q or from Q to P.

To illustrate the meaning of the terms " reversible " and " irreversible ", let us consider some particular changes. Whenever heat is produced by friction, as for example in Joule's paddle-wheel experiment, the process is clearly irreversible. For this reason it was necessary to assume in the ideal heat engine that all movements, such as the motion of the piston in the cylinder, could be made without friction. Whenever two fluids, whether liquids or gases, mix together as in the process of diffusion, it is evident that the reverse process cannot be effected under normal conditions. From the standpoint of the molecular theory, it is clear that separation could only be brought about by operating on individual molecules. Again, the passage of heat from a body at a high temperature to another at a low temperature, whether by conduction or by radiation, is strictly speaking irreversible. It will be remembered that in dealing with Carnot's

cycle we had to suppose that all *differences* of temperature were infinitesimal.

On the other hand, such changes as the expansion or compression of the working substance may be made reversible under certain conditions. The reversible process is in such cases a limiting or ideal case. This type of change was noticed in connection with Carnot's engine when the changes in volume occurred infinitely slowly.

The second law of thermodynamics. The first law of thermodynamics states the equivalence of heat and energy. The second law is less easy to grasp ; it is concerned with the *method* by which heat can be transformed into mechanical work, and the *direction* in which natural processes occur.

Although it is sometimes stated that heat and work are equivalent, there is an essential difference between heat and other forms of energy. A quantity of any other kind of energy can be completely converted into heat, but the conversion of heat into another form of energy is restricted by certain conditions. This was expressed by Willard Gibbs in the phrase, " There is only a one-sided convertibility ".

The kinetic molecular theory of gases is of assistance in understanding this difference. To obtain mechanical work, as for instance when the explosion sets in motion the piston of a gas engine, it is necessary that there should be some degree of orderly movement of the gas molecules in the direction of motion of the piston. Heat energy is largely the disorderly movement of the molecules. The problem is to convert irregular motion into regular motion !

The second law of thermodynamics has been expressed in a number of different ways, perhaps the most familiar being the statement of Clausius. " It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low, to one at a high temperature." Or, " heat cannot of itself, i.e. without the performance of work by some external agency, pass from a cold to a warm body ". In other words : " It is not possible in a cyclic process to convert heat into work without at the same time transferring a quantity of heat from a warmer to a colder body " .

Kelvin stated the second law in a somewhat different form. Suppose we are dealing with only two bodies, a hot reservoir and a cold reservoir. Then, according to Kelvin, it is impossible to obtain work *continuously* by using up the heat of the colder of the two bodies. In more general terms, " it is impossible by means of inanimate material agency to derive mechanical effect (continuously) from any portion of matter by cooling it below the temperature of the coldest of surrounding objects ".

It is proverbially difficult to prove a negative, and this second law must be regarded as a statement which is in harmony with the result of our general experience. It should be carefully noticed that the law has reference to a machine which works in cycles.

Carnot's theorem. Assuming the truth of the second law, we may deduce two important results which are usually taken together to constitute **Carnot's theorem.**

(*a*) No engine can be more efficient than a reversible engine working between the same limits of temperature.

(*b*) All reversible engines working between the same limits of temperature have the same efficiency.

Let us consider the state of affairs represented diagrammatically in Fig. 225, and suppose that we have a source of heat at a certain definite temperature θ_1, and a sink at some lower temperature θ_2. We assume there are two engines R and S, working between these temperatures. Of these two engines R is reversible, but S is not. We require to prove the theorem which states that S cannot be more efficient than R. Let us suppose that S *is* more efficient than R. The two engines may be so constructed, by suitably arranging the quantity of the working substance, that they draw the same quantity of heat (Q_1 say) from the source. If S does more work than R, it must yield less heat to the sink; in other words, if R yields a quantity of heat Q_2 to the

FIG. 225. TWO IDEAL HEAT ENGINES, R AND S, COUPLED TOGETHER

sink, S yields some smaller quantity $Q_2 - q$. The engine R is, by hypothesis, reversible. Consequently S may be used to drive R backwards. When the two engines are coupled up, with R working backwards, the source remains unaffected, but R takes from the cold reservoir a quantity of heat Q_2, and S yields a quantity $Q_2 - q$ to this reservoir. Thus there is a quantity of work obtained from the compound engine in each cycle equal to q, and there is a corresponding withdrawal of heat from the cold reservoir. This result is contrary to the second law of thermodynamics, for the law states that in a cyclic process work cannot be obtained by withdrawing heat from the colder of the two bodies under consideration. Hence our hypothesis is incorrect, and we conclude that S cannot be more efficient than R, that is a non-reversible engine cannot have its efficiency greater than that of a reversible engine working between the same temperatures.

The second part of Carnot's theorem (*b*) tells us that all *reversible* engines must have the same efficiency. This may be proved by an

argument on the same lines as before, calling the two engines R_1 and R_2. We begin by assuming that R_1 is more efficient than R_2, and show, as in the previous case, that this implies a failure of the second law. In the same way we may show that R_2 cannot be more efficient than R_1. Consequently all reversible engines working between the temperatures θ_1 and θ_2 have the same efficiency, and therefore $\dfrac{Q_1 - Q_2}{Q_1}$, which is by definition the efficiency, is the same for all such ideal engines.

THE ABSOLUTE SCALE OF TEMPERATURE AND THE ABSOLUTE ZERO OF TEMPERATURE

Absolute temperature. Any property which depends *only* on temperature can be used to define a scale of temperature. As examples of such properties we may cite the expansion of any material substance, whether it be a solid, a liquid or a gas, the electrical resistance of a conductor, or the thermal electromotive force arising from different conductors in contact. The method of defining the scale has been described in Chapter II. But in all the cases mentioned the temperature scale obtained will depend on the properties of the particular substance selected.

Lord Kelvin showed that it was possible to define a temperature scale which deserves the title *absolute*, because it does *not* depend on the properties of any particular substance. This possibility is a consequence of Carnot's theorem, which may be expressed in the form : " The efficiency of all *reversible* Carnot engines, working between two assigned temperatures, is a function of those two temperatures alone ". In this statement the nature and properties of the working substance do not enter. The sole condition attached to the Carnot engine is that it should be *reversible*, and this condition depends not on the working substance employed but on the way in which the various operations in the cycle are carried out. We must now consider how it is possible to define a temperature scale by making use of Carnot's theorem.

Kelvin's absolute scale of temperature. We shall use the Greek letter θ to denote the temperature measured on *any* scale, that is without specifying any particular method of measuring temperature, and call the temperatures of the source and the condenser θ_1 and θ_2 respectively. In the case of a reversible engine, the efficiency, $\dfrac{Q_1 - Q_2}{Q_1}$, is independent of the nature of the working substance. It must, therefore, be determined by the two temperatures between which the engine works. This means that $\dfrac{Q_1 - Q_2}{Q_1}$ is some function f of the two temperatures θ_1 and θ_2, where θ_1 is higher than θ_2.

Thus

$$\frac{Q_1 - Q_2}{Q_1} = f(\theta_1, \theta_2),$$

or

$$1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2).$$

Clearly $\frac{Q_2}{Q_1}$, and therefore also $\frac{Q_1}{Q_2}$, must be a function of these two temperatures θ_1 and θ_2. Accordingly, we may write $\frac{Q_1}{Q_2}$ in the form

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2).$$

It should be noticed carefully that this new function is the ratio of the *larger* of the two quantities of heat to the *smaller*. Now, if we have a reversible engine working between the limits θ_2 and θ_3, where θ_2 is higher than θ_3, we find by similar reasoning that in this engine $\frac{Q_2}{Q_3}$ is, in accordance with Carnot's theorem, the *same* function of θ_2 and θ_3, or

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3).$$

Multiplying these two results together, we obtain

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3).$$

But the quantity on the left-hand side must be capable of representation in the same form as before, that is, by $F(\theta_1, \theta_3)$, for we may employ a reversible engine working between the temperatures θ_1 and θ_3. Thus we find that

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3).$$

This equation is described as a *functional* equation.

Now we must consider what possible form the function F can take to satisfy this condition. On the left-hand side of the equation we have θ_1 and θ_3 only, and θ_2 is *not* present. On the right-hand side, θ_2 is present in each of the two factors, and it is clear that θ_2 must disappear from this side of the equation. To ensure this, the function $F(\theta_1, \theta_2)$ must be of the form

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)},$$

and

$$F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)},$$

ϕ being another function.

For, in this case,

$$F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \times \frac{\phi(\theta_2)}{\phi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_3)}.$$

The fact that the function $F(\theta_1, \theta_2)$ can be expressed by means of the equation

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

carries with it important consequences.   For it involves the simple result

$$\frac{Q_1}{Q_2} = \frac{\phi(\theta_1)}{\phi(\theta_2)}.$$

The form of the function $\phi(\theta)$ is left undetermined, but we may, if we choose, take $\phi(\theta)$ itself to represent the temperature of the working substance.   Let us, then, agree to employ $\phi(\theta)$ as a measure of temperature, and for convenience let us represent $\phi(\theta)$ by the Greek letter τ, where τ may be called " temperature on the absolute scale ".

We now have

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2}.$$

This new scale of temperature is such that any two temperatures on it bear to each other the same ratio as the quantities of heat taken in and ejected by a reversible engine working between these temperatures. Employing this scale we obtain :

$$\text{efficiency} = \epsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{\tau_1 - \tau_2}{\tau_1}.$$

We notice that if we put $\tau_2 = 0$ in this formula, the efficiency is equal to unity.   For clearly if the heat ejected by an engine at the lower temperature is zero, *all* the heat Q_1 taken from the source will be converted into work.

Graphical representation of the absolute scale.   We have obtained the

relation $\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2}$, where Q_1 and Q_2 represent the quantities of heat taken in and rejected by a reversible engine working between two temperatures specified by τ_1 and τ_2.   This relation means that the numbers representing any two temperatures on the thermodynamic scale are proportional to the quantities of heat taken in or liberated at those temperatures. This result is independent of the working substance employed, and thus, as Lord Kelvin showed in 1848, we may obtain an *absolute* scale of temperature defined by

FIG. 226.   GRAPHICAL REPRESENTATION OF THE ABSOLUTE SCALE OF TEMPERATURE

this equation.   There is a simple graphical method of representing this absolute scale of temperature.   It is illustrated in Fig. 226.

Take any two adiabatics AA', BB' for any arbitrary substance, and draw any isothermal A_1B_1. Corresponding to the change from A_1 to B_1 there will be some quantity of heat Q_1 either absorbed or ejected. Now take some lower isothermal A_2B_2, and let the corresponding quantity of heat be Q_2. The area $A_1B_1B_2A_2 = Q_1 - Q_2$ represents the work done in the cycle. Now choose an isothermal A_3B_3 so that the area $A_2B_2B_3A_3 = A_1B_1B_2A_2$. Proceed in the same way and obtain a number of isothermals A_3B_3, A_4B_4, etc. Then from the mode of construction it follows that

$$Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4 = \ldots .$$

If we agree to take

$$\frac{Q_1}{\tau_1} = \frac{Q_2}{\tau_2} = \frac{Q_3}{\tau_3} = \ldots ,$$

it follows that

$$\tau_1 - \tau_2 = \tau_2 - \tau_3 = \tau_3 - \tau_4 \ldots ,$$

that is to say, the isothermals drawn in this way correspond to *equal* differences of temperature. Now we may choose $\tau_1 - \tau_2$ to represent 1° of temperature. Then $\tau_2 - \tau_3$ will also be 1°, and $\tau_1 - \tau_3$ will be two degrees, and so on. It appears then that on Lord Kelvin's scale the number of degrees of temperature between AB and any other temperature $A'B'$ is proportional to the area $ABB'A'$. So far, the size of the degree has been left arbitrary, but we may choose our new scale so that there are 100 degrees between the freezing point and the boiling point of water.

Absolute zero of temperature. In general we have $\dfrac{Q}{Q'} = \dfrac{\tau}{\tau'}$.

The absolute zero of temperature corresponds to $Q' = 0$. Since the efficiency is $\dfrac{Q - Q'}{Q}$, we see that when $Q' = 0$ the efficiency is unity.

The absolute zero of temperature is the temperature of the condenser of an ideal heat engine when the efficiency of the engine is unity. This means that all the heat taken from the source is converted into work. We cannot conceive that more heat can be converted into work than is drawn from the source. This shows that τ cannot be negative, and therefore the temperature corresponding to $\tau = 0$ is the lowest possible temperature. It should be noticed that this absolute zero of temperature is independent of the properties of any particular substance.

Let us agree to use the scale which has an interval of one hundred degrees between the freezing point and the boiling point of water.

Let τ_B = temperature of the boiling point of water,

and τ_F = temperature of the freezing point of water.

Then $\tau_B = \tau_F + 100.$

From experiments on gases Kelvin calculated that

$$\frac{\tau_B}{\tau_F} = \frac{Q_B}{Q_F} = 1 \cdot 366, \text{ approximately.}$$

Hence
$$\frac{\tau_F + 100}{\tau_F} = 1 \cdot 366 ;$$

$$\therefore \ 1 + \frac{100}{\tau_F} = 1 \cdot 366 ;$$

$$\therefore \ \frac{100}{\tau_F} = 0 \cdot 366 ;$$

$$\therefore \ \tau_F = \frac{100}{0 \cdot 366} = 273° \text{ approximately} ;$$

and
$$\tau_B = \tau_F + 100 = 373° \text{ approximately.}$$

Thus on the absolute thermodynamic scale we may take the freezing point of water as 273° and the boiling point as 373°.

APPLICATIONS OF CARNOT'S CYCLE

Carnot's cycle for a perfect gas. We have considered already the conception of an ideal or perfect gas. For our present purpose it will be sufficient to assume that the equation $pv = RT$ may be applied *exactly*, where T is the temperature measured on the scale of the gas thermometer. Also it will be assumed that the equation of an adiabatic is $pv^\gamma = $ constant, where γ is the ratio of the two specific heats of a gas.

Consider a cycle composed of two isothermals and two adiabatics. The indicator diagram is shown in Fig. 227. The points B and C are on the same isothermal, corresponding to some temperature T_1 (say) ; consequently

FIG. 227. CARNOT'S CYCLE WITH A PERFECT GAS FOR THE WORKING SUBSTANCES

$$p_c v_c = p_b v_b = RT_1. \quad \dots\dots\dots\dots\dots\dots\dots(1)$$

The points A and D are on the same isothermal at a temperature T_2 ; consequently

$$p_d v_d = p_a v_a = RT_2. \quad \dots\dots\dots\dots\dots\dots\dots(2)$$

Next we notice that the points C and D are on the same adiabatic ; consequently

$$p_c v_c{}^\gamma = p_d v_d{}^\gamma. \quad \dots\dots\dots\dots\dots\dots\dots\dots(3)$$

The points B and A are on the same adiabatic; consequently

$$p_b v_b{}^\gamma = p_a v_a{}^\gamma. \qquad \qquad \text{(4)}$$

Here, then, we have four equations connecting the various pressures and volumes.

Consider next the quantities of heat taken in or given out by the working substance. In the change from B to C a quantity of heat, Q_1, is taken in, which is equal to $\int_b^c p\, dv$. In this isothermal change $pv = RT_1$, and therefore $p = RT_1/v$.

Hence

$$\begin{aligned}
Q_1 &= \int_b^c RT_1 \frac{dv}{v} \\
&= RT_1 \int_b^c \frac{dv}{v} \\
&= RT_1 \left[\log_e v\right]_b^c \\
&= RT_1 (\log_e v_c - \log_e v_b) \\
&= RT_1 \log_e (v_c/v_b). \qquad \qquad \text{(5)}
\end{aligned}$$

In the same way we can calculate the quantity of heat, Q_2, which is given out in the isothermal change from D to A, and we obtain

$$Q_2 = RT_2 \log_e (v_d/v_a). \qquad \qquad \text{(6)}$$

We are interested in the ratio of Q_1 to Q_2, and this is given by

$$\frac{Q_1}{Q_2} = \frac{T_1 \log_e (v_c/v_b)}{T_2 \log_e (v_d/v_a)} . \qquad \qquad \text{(7)}$$

This result may be simplified by making use of equations (1) to (4).

We start with equations (3) and (4) and divide (3) by (4). Then we obtain

$$\frac{p_c v_c{}^\gamma}{p_b v_b{}^\gamma} = \frac{p_d v_d{}^\gamma}{p_a v_a{}^\gamma} . \qquad \qquad \text{(8)}$$

From equations (1) and (2), we find

$$\frac{p_c v_c}{p_b v_b} = \frac{p_d v_d}{p_a v_a} . \qquad \qquad \text{(9)}$$

When we divide (8) by (9), we get

$$\left(\frac{v_c}{v_b}\right)^{\gamma-1} = \left(\frac{v_d}{v_a}\right)^{\gamma-1},$$

or

$$\frac{v_c}{v_b} = \frac{v_d}{v_a} . \qquad \qquad \text{(10)}$$

Consequently equation (7) becomes

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} . \qquad \qquad \text{(11)}$$

Now, on the thermodynamic scale of temperature, we know that

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2} . \qquad \qquad \text{(12)}$$

Comparing the two results (11) and (12), we see that $\frac{T_1}{T_2} = \frac{\tau_1}{\tau_2}$, or in other words, **the gas scale of temperature represented by T agrees with the absolute scale represented by τ.**

Also, the absolute zero of Kelvin's scale will agree with the absolute zero of the gas scale. It should be noticed that the gas scale here referred to is the scale of an ideal or perfect gas. An actual gas will furnish us with a scale of temperature which is approximately, but not exactly, the same as that represented by T.

In experimental work, the standard thermometric scale adopted by the International Committee of Weights and Measures (1887) is that of the constant volume hydrogen thermometer. It is possible to determine the corrections which must be applied to this international scale, depending as it does on the properties of a real gas, to give the corresponding reading on the scale of the perfect gas thermometer which is, as we have seen, in agreement with the thermodynamic scale of temperature.*

Reduction of the readings of an air thermometer (or a thermometer containing an actual gas) to the thermodynamic scale. Let t be the temperature on the air thermometer corresponding to the Kelvin temperature T. Our problem is to express t in terms of T.

Let c_p' be the specific heat at constant pressure determined when using an air thermometer.

$$c_p = \frac{dQ}{dT}, \quad c_p' = \frac{dQ}{dt}; \quad \therefore \; c_p = c_p' \frac{dt}{dT}.$$

The Joule-Thomson equation (p. 689) may be written

$$c_p \frac{dT}{dp} = T\left(\frac{\partial v}{\partial T}\right)_p - v.$$

$$\left(c_p' \frac{dt}{dT}\right)\left(\frac{aT}{dt}\frac{dt}{dp}\right) = T\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{dT} - v.$$

$$c_p' \frac{dt}{dp} + v = T\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{dT}.$$

$$\therefore \int \frac{dT}{T} = \int \frac{\left(\dfrac{\partial v}{\partial t}\right)_p dt}{c_p' \dfrac{dt}{dp} + v}.$$

$$\therefore \; \log\left(\frac{T_2}{T_1}\right) = \int_{t_1}^{t_2} \frac{\left(\dfrac{\partial v}{\partial t}\right)_p dt}{c_p' \dfrac{dt}{dp} + v}.$$

* For such a table of corrections see page 13 of Roberts's *Heat and Thermodynamics*.

The quantities which occur on the right-hand side can be found by experiment using an air thermometer, and the integral can be evaluated by a graphical method. Thus $\dfrac{T_2}{T_1}$ or the *ratio* of two temperatures on the absolute scale can be found. If we agree to take 100 divisions of the absolute scale between melting point and boiling point, it is found that $T_0 = 273 \cdot 16$. The absolute thermodynamic temperature T corresponding to any temperature t on the air thermometer can therefore be found.

For a more complete discussion of the second law of thermodynamics than is possible here, reference may be made to Planck's *Thermodynamics*.

WORKED EXAMPLES

1. *An engine works in a Carnot's cycle between the temperatures* 100° C. *and* 0° C.; *if the work done in the cycle is* 1200 *kilogram-metres, find how much heat, measured in calories, is taken in at the higher temperature.*

(St. A. U. M.A. Special, 1937.)

Let Q_1 = heat taken in at temperature 100° C. = 373° K.,

and Q_0 = heat rejected at temperature 0° C. = 273° K.

Then we may write $\dfrac{Q_1}{Q_0} = \dfrac{373}{273}$.

Work done = 1200 kilogram-metres

$$= 1 \cdot 2 \times 10^3 \times 10^3 \times 10^2 = 1 \cdot 2 \times 10^8 \text{ gm. cm.}$$

$$= 1 \cdot 2 \times 10^8 \times g \text{ ergs.}$$

If A = work done (measured in ergs), $Q = Q_1 - Q_0$ = heat expended (measured in calories), and J is Joule's equivalent = $4 \cdot 18 \times 10^7$ ergs/calorie, we can apply the first law of thermodynamics, and write $A = JQ$.

$$\therefore \ 1 \cdot 2 \times 10^8 \times 981 = 4 \cdot 18 \times 10^7 (Q_1 - \tfrac{273}{373}Q_1)$$

$$= 4 \cdot 18 \times 10^7 (\tfrac{100}{373}Q_1) \ ;$$

$$\therefore \ Q_1 = \frac{1 \cdot 2 \times 10^8 \times 981 \times 373}{4 \cdot 18 \times 10^7 \times 100} = 1 \cdot 08 \times 10^4 \text{ calories.}$$

2. *Calculate the efficiency of a reversible heat engine working between the temperatures* 167° C. *and* 57° C.

The efficiency (ϵ) is defined as the ratio $\dfrac{\text{work done}}{\text{heat taken in from the source}}$.

If we express this in symbols, we may write

$$\epsilon = \frac{Q_1 - Q_2}{Q_1}.$$

On the thermodynamic scale of temperature this becomes

$$= \frac{\tau_1 - \tau_2}{}$$

or, on the gas scale of temperature,

$$\epsilon = \frac{T_1 - T_2}{T_1}.$$

Now $T_1 = 167°\,C. = 440°\,K.,$

and $T_2 = 57°\,C. = 330°\,K.;$

$$\therefore\ \epsilon = \frac{440 - 330}{440} = \frac{110}{440} = 0\cdot25.$$

QUESTIONS

Chapter XXIX

1. Write a short essay on the second law of thermodynamics.   (E.U., M.A.)

2. Define a Carnot cycle, paying special attention to the conditions for reversibility.
Show that the efficiency of a heat engine working in a Carnot cycle can only depend on the temperatures between which the engine is working.   (L.U., B.Sc.)

3. Explain what is meant by an ideal heat engine and by a Carnot cycle. If the working substance in a Carnot cycle is a perfect gas, investigate an expression for the ratio of the heat taken in at temperature T_1 on the gas scale to the heat given out at a lower temperature T_2.

4. Describe the various stages in a Carnot cycle performed with a perfect gas as the working substance, and show that the temperature scale for such a gas agrees with the thermodynamic scale.   (E.U. Inter. Hons.)

5. Describe the cycle of operations known as Carnot's cycle. Find the efficiency, using a perfect gas as the working substance.
Give an example of the application of Carnot's cycle to the solution of a problem in heat.   (E.U. Inter. Hons.)

6. Describe the operations involved in a Carnot cycle and explain how such a cycle could be used in refrigeration. What modifications of it are introduced in practical refrigeration?   (L.U., B Sc.)

7. Explain what is meant by an ideal heat engine, and by the term efficiency. Describe in detail the performance of a Carnot cycle by such an engine. Indicate the theoretical importance of this process, and state the conditions for maximum efficiency.

8. Give a *brief* description of Carnot's cycle, explaining its theoretical importance.
An engine works in a Carnot's cycle between the temperatures 100° C. and 0° C. Calculate the work done in the cycle in ergs if the quantity of heat taken in at the higher temperature is 10^4 calories.

9. An engine works in a Carnot cycle between the temperatures 100° C. and 15° C.; if the work done in the cycle is 400 kilogram-metres, how much heat, measured in calories, is taken in at the upper temperature?

10. What do you mean by a reversible process?
Show that all reversible engines working between the same two temperatures have the same efficiency, and that this is not less than that of any other engine working between these temperatures.

11. Making use of a suitable axiom, show that the efficiency of a reversible engine is determined only by the temperatures of the source and sink.
Explain how this result may be made to lead to the establishment of an absolute scale of temperature.   (L.U., B.Sc.)

12. Write an account of Kelvin's scale of absolute temperature.

13. Define the absolute or thermodynamic scale of temperature, and show that this scale agrees with that of the perfect gas thermometer.

14. Explain what you understand by the terms " absolute temperature " and " perfect gas ". Show that the temperature intervals on the Kelvin thermodynamic work scale are proportional to those on the perfect gas scale.   (L.U., B.Sc.)

15. Prove that the scale of a perfect gas thermometer agrees with the absolute thermodynamic scale of Lord Kelvin.

Explain briefly how a numerical value can be found for the " ice-point " on the Kelvin scale.   (St. A. U.)

CHAPTER XXX

ENTROPY

FROM the consideration of energy in its various forms and the relation between heat energy and mechanical work, we must now turn to a somewhat more difficult concept—that of **entropy**. It is well to remember that the term energy, when first introduced into science, gave rise to much discussion and some considerable time elapsed before the distinction between force and energy became so familiar as it is at the present time. By means of suitable analogies which will be described in this chapter it is possible to obtain tolerably clear ideas of this new concept which some of the masters of physical science have placed on an equality with energy in intrinsic importance.

We have seen that on the indicator or p-v diagram a series of **isothermals** may be drawn (Fig. 228), these curves being distinguished from one another by their respective temperatures. We may go further, and so choose the isothermals that the difference between the temperatures of consecutive curves has some assigned value, say one degree. Temperature then may be regarded as a property distinguishing one isothermal from another.

We may also draw on the indicator diagram a number of **adiabatics** A_1, and the question arises: How can we distinguish between the different adiabatics? In going from one adiabatic to another, say from the adiabatic A_1 to the adiabatic A_2, a certain quantity of heat Q is either absorbed or rejected, but this quantity Q is *not* constant as we go from the first adiabatic to the second. It depends on the temperature at which the
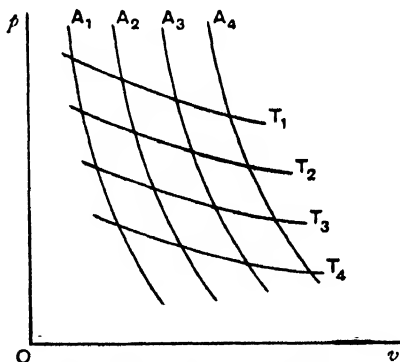
FIG. 228. ADIABATICS AND ISOTHERMALS

change takes place. Using Lord Kelvin's **absolute** scale of temperature, in which temperature is represented by $T°$ K. we have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} \cdots .$$

If we consider the interval on an isothermal between two given adiabatics Q_1 is the quantity of heat appropriate to the isothermal T_1; Q_2 is the quantity of heat appropriate to the isothermal T_2; Q_3 to T_3, and so on. We see then that Q/T is the same *whatever isothermal is chosen* for making the transition from the adiabatic A_1 to the adiabatic A_2. Thus Q/T may be regarded as a property determined by the two adiabatics A_1 and A_2, and this quantity may be taken as a measure of the difference between these two adiabatics. Accordingly we define the **change of entropy** between a given pair of adiabatics A_1 and A_2 as equal to the value of Q/T in an isothermal change from the adiabatic A_1 to the adiabatic A_2. We shall see later that it is not essential that the change should be isothermal, the necessary condition is that it should be reversible. Expressed in symbols, this definition for change of entropy is

$$S_2 - S_1 = \frac{Q_{12}}{T},$$

where S is used to denote entropy, in accordance with the recommendation of an International Conference on Physics (London, 1934). The older text-books employed the symbol ϕ in place of S.

From the standpoint here adopted, we see that entropy measures the " rank " of an adiabatic in the same way that temperature may be regarded as measuring the " rank " of an isothermal.

We know that by using Kelvin's absolute scale of temperature the areas of successive Carnot cycles between two selected adiabatics (A_1 and A_2) are equal for equal differences of temperature. In a similar way we may mark off a series of adiabatics A_1, A_2, A_3, A_4, ... , so as to make the areas included between two selected isothermals (T_1 and T_2) and consecutive adiabatics equal. Then equal differences of entropy would correspond to equal areas on the diagram.

In measuring energy we are concerned in practice with differences of energy rather than with an absolute amount of energy. In the same way in thermodynamics we are usually concerned with differences of entropy rather than with the absolute value of entropy.

When a transition takes place from a state A to a state B at constant temperature T, the change of entropy $S_B - S_A = Q/T$. We shall now consider some examples of such changes at constant temperature.

Numerical examples.

(1) *Find the difference in entropy between* 1 *gram of water and* 1 *gram of ice at* 0° *C. and* 1 *atmosphere pressure if the latent heat of fusion is* 80 *calories per gram.*

A quantity of heat, $Q = 80$ calories, is given to 1 gram of ice at absolute temperature $T = 273°$ to convert it into water, without any change of temperature taking place.

$$S_B - S_A = \text{change of entropy} = \frac{80}{273} \text{ calories per degree centigrade.}$$

$$= 0.293 \text{ calories per } 1° \text{ C.}$$

We notice that the units employed in measuring entropy are the same as those used in expressing the thermal capacity of a body.

(2) *Find the difference in entropy between* 1 *gram of water and* 1 *gram of steam at* 100° *C. and at atmospheric pressure, if* $L \backsim 540$ *calories per gram.*

$$S_B - S_A = \frac{540}{273 + 100} = \frac{540}{373} = 1.448 \text{ calories per } 1° \text{ C.}$$

(3) *The melting point of lead is* 327° *C. and the latent heat of fusion is* 5.86 *calories per gram. Calculate the entropy change when* 4 *gram-molecules of lead are fused. The atomic weight of lead* $\simeq 207$.

Since lead is monatomic, 4 gram-molecules are $4 \times 207 = 828$ gm.

Therefore the heat absorbed when 4 gram-molecules of lead are fused $= Q = 5.86 \times 828 = 4852$ calories.

Melting point of lead $= 327°$ C. Hence $T = (327 + 273)°$ K. $= 600°$ K.

Thus the change of entropy $= S_B - S_A = \frac{Q}{T} = \frac{4852}{600} = 8.1$ calories per $1°$ C.

Mathematical expression for change of entropy. The concept of entropy introduced in this simple way may be defined more rigorously as follows :

If an elementary quantity of heat δQ is *added* to a system *by a reversible process* at a mean temperature T, then $\delta Q/T$ is called the *increase* in entropy of the system and may be denoted by δS. (Some writers call the increase in entropy $\delta\phi$.) Similarly if an amount of heat δQ is withdrawn from the system at a mean temperature T, there is a decrease in the entropy of the system equal to $\delta Q/T$. Hence, in general,

$$\delta S = \delta Q/T.$$

For an infinitesimal change

$$dS = dQ/T.$$

The difference in notation between dQ and dS arises from the fact that dQ is not a perfect differential, but dS is a perfect differential.* The factor $1/T$ which multiplies dQ is known as an integrating factor and converts dQ into a perfect differential. This implies that in going from

* For a definition of a perfect differential, see Chapter XXXII, p. 649.

a point A on the indicator diagram to a neighbouring point B the change in entropy is independent of the path followed.

From the definition of difference of entropy $dS = dQ/T$, it follows that in a finite change of the system

$$S_B - S_A = \int_A^B \frac{dQ}{T}.$$

The use of this formula is illustrated in the following problem.

Find the difference of entropy for a given mass m of a solid between two temperatures T_A and T_B ($T_B > T_A$), assuming the specific heat, c, constant between those temperatures, and no change of state to occur.

With these assumptions $dQ = mc\,dT$, and

$$S_B - S_A = \int_A^B mc\,\frac{dT}{T} = mc \int_A^B \frac{dT}{T} = mc \left[\log_e T \right]_A^B$$
$$= mc \log_e (T_B/T_A).$$

Numerical Example.

Find the difference of entropy between 1 gram of water at 0° C. and 1 gram of water at 100° C., the specific heat of water being assumed constant and equal to 1.

The corresponding temperatures on the absolute scale are 273° K. and 373° K. respectively.

For a rise of temperature dT, the heat communicated is

$$dQ = 1 \times dT \text{ calories.}$$

$$S_B - S_A = \int_{T=273}^{T=373} dT/T = \left[\log_e T \right]_{273}^{373} = \log_e \frac{373}{273} = \left(\log_{10} \frac{373}{273} \right) \left(\log_e 10 \right)$$
$$= (2 \cdot 5717 - 2 \cdot 4362)(2 \cdot 3026) = 0 \cdot 1355 \times 2 \cdot 3026$$
$$= 0 \cdot 312 \text{ calorie per 1° C.}$$

We have already found (p. 617) that the change of entropy when 1 gram of ice at 0° C. is melted is 0·293 calorie per 1° C., and also that the change of entropy when 1 gram of water at 100° C. is converted into steam at 100° C. is 1·448 calories per 1° C. Summing the three results we find that the change of entropy when 1 gram of ice at 0° C. is converted into steam at 100° C. is 2·053 calories per 1° C.

SOME PHYSICAL ANALOGIES OF ENTROPY

Entropy has been called the " ghostly quantity " because of the difficulty experienced in realising its nature. The mathematician may be content to regard it as a function defined by an equation, but for the physicist or engineer who finds the conception of entropy difficult to grasp because of its intangible character it may be of assistance to point out some corresponding physical quantities. We therefore consider some analogies likely to be of service in understanding this thermal

quantity, though we must always be careful not to pursue analogies too far. " The more shadowy the conception to be visualised, the greater the need of a definite material analogy."

We have by definition

$$\text{change of entropy} = \frac{\text{heat energy}}{\text{temperature}},$$

and consequently heat energy has the same physical dimensions as the product of entropy and absolute temperature.

We are familiar with other cases where energy appears as the product of two factors. For example, potential energy due to the force of gravity is given by the formula

$$\text{potential energy} = Mgh,$$

and this mechanical energy may be measured in dynamical units, such as foot-poundals, or in gravitational units, such as foot-pounds. Thus gravitational energy is proportional to mass and also to height above some zero level. If then temperature is regarded as equivalent to height above a certain level, and we must remember that the temperature here involved is measured from the absolute zero, we see that entropy is analogous to mass or inertia.

Again, we know that in electrostatics the electrical energy of a charged conductor is proportional to the product of the charge and the potential. If then we regard electric potential as analogous to temperature, we are led to look upon electric charge as a quantity corresponding to entropy.

Heat energy may conveniently be regarded as equivalent to the kinetic energy of the ultimate particles of which matter is composed, although it should be remembered that it may also include potential energy. We obtain a very useful analogy, which may be of service in elucidating the nature of entropy, if we think of the kinetic energy as due to rotation. It may be recalled that Rankine was able to make considerable progress in the theory of heat by using the hypothesis of *molecular vortices*, and in fact it was in the course of this work that he introduced a mathematical function equivalent to entropy.

When Rankine was compelled to abandon the theory based on molecular vortices, he called on all those who taught the subject to try and find some popular means of illustrating the second law. An attempt so to do was made by Osborne Reynolds * in 1883.

" The general idea of the mechanical condition which we call heat is, that the particles of matter are in active motion ; but it is the motion of the individuals in a mob, with no common direction or aim. Rankine assumed the motion to be rotatory, but it now appears more probable that the motion of the particles is oscillatory, undulatory, rotatory and

* *Scientific Papers*, Vol. II, p. 138.

all kinds of motion, whatsoever ; so that the communication of heat to matter means the communication of internal agitation—mob agitation If, then, we are to make a machine to act the part of hot matter, we must make a machine to perform its work in virtue of internal promiscuous motion amongst its parts."

As an illustration Osborne Reynolds instances the possibility of raising a bucket by violently shaking the upper end of a heavy rope or chain. A modification of the illustration is afforded by a kind of chain composed of a series of parallel horizontal bars of wood connected and suspended by two strings. " By giving a circular oscillation to the upper bar, the whole apparatus is set into a twisting motion (agitation) ; the strings are continually bent, and the vertical length of the whole system is shortened."

Reynolds also refers to " the principle of the kinetic machine—long ago applied by Watt ". " The common governor of a steam engine acts by kinetic elasticity, which elasticity, depending on the speed at which the governor is driven, enables the governor to contract as the speed increases. The motion of the governor is not of the form of promiscuous agitation, but, though systematic, all the motion is at right angles to the direction of operation, so that the *principle of its action is the same.*"

" These kinetic examples of the action of heat must not be expected to simplify the theory, except in so far as they give the mind something definite to grasp : what they do is to substitute something we can see for what we can barely conceive."

The employment of rotational motion in illustration of the properties of entropy was developed by A. M. Worthington and S. G. Wheeler * in the Royal Naval Engineering College, Devonport.

Kinetic energy of rotation. Kinetic energy due to rotation is given by the expression $\frac{1}{2}I\omega^2$, that is, it depends on two factors, the **rotational inertia** (or moment of inertia) I, and ω^2, **the square of the angular velocity.** It should be noticed that the rotational inertia I is not necessarily constant, since it depends on the *arrangement* of the masses. Thus in the governor of a steam engine, the moment of inertia varies with the speed of rotation. The transformation of heat into work does not, as a rule, take place without a change in the thermal inertia. It is possible to visualise a mechanism composed of revolving masses similar to the " governor balls " in which such a change in rotational inertia may take place.

By using such analogies we may think of the " Entropy " or " Thermal Inertia " of a system as a quantity which bears to heat motion a similar relation to that which mass and rotational inertia bear to linear motion and rotation respectively.

Speaking broadly, **heat energy** may be regarded as composed of two factors, thermal inertia or **entropy**, S, **and temperature** on the absolute scale, T.

* Wheeler, *Entropy as a Tangible Conception* (Crosby Lockwood, 1921) ; *Nature*, Vol. 109, p. 404, 1922.

Entropy as a function of the state of a substance. The entropy of a substance is a function of its actual state, *and does not depend on previous conditions.*

" It is chiefly because the entropy of a substance is a definite function of the state (like the temperature, or the pressure, or the volume, or the internal energy) that the notion of entropy is important in engineering theory. The entropy of a substance is usually reckoned per unit of mass, and numerical values of it reckoned in this manner are given in tables of the properties of steam and of the other substances which are used in heat engines and refrigerating machines.

" But we may also reckon the entropy of a body as a whole when the state of the body is fully known, or the change of entropy which a body undergoes as a whole when it takes in or gives out heat. And we may also reckon the total entropy of a system of bodies by adding together the entropies of the several bodies that make up the system " (Ewing).

When a body passes from one state to another, the entropy which it gains depends solely on the initial and final states. This important result we must now consider in detail.

CHANGE OF ENTROPY IN A CYCLE

Change of entropy in a Carnot cycle. Let us consider the change in entropy in a reversible cycle. At present we consider *only* reversible changes. The simplest case is the simple cycle of Carnot, where we have two isothermals and two adiabatics, as in Fig. 229. In this simple cycle we have

$$Q_1/T_1 = Q_2/T_2, \text{ or } Q_1/T_1 - Q_2/T_2 = 0.$$

Here Q_1 is the heat taken from the source at temperature T_1, and Q_2 is the heat given to the condenser or sink at temperature T_2. We may refer these quantities of heat to the working substance which goes through the cycle instead of to the reservoirs of heat. Let us agree to reckon heat taken in by the substance

FIG. 229. CHANGE OF ENTROPY
IN A CARNOT'S CYCLE

as positive, and heat given out by the substance as negative. Then Q_1 is to be considered a positive quantity, while Q_2 is to be considered a negative quantity, and the equation becomes $Q_1/T_1 + Q_2/T_2 = 0$. As we are considering heat taken in as positive, Q/T represents the *increase* in the entropy of the working substance, and this equation expresses the fact that in the simple Carnot cycle the *total* increase of entropy is zero.

In the original treatment of the simple cycle by Sadi Carnot the caloric theory of heat was employed, and it was assumed that all the caloric absorbed from the source was rejected to the condenser of the engine. This we know is not in accord with the dynamical theory of heat, according to which it is the *difference* between the two amounts of heat that is converted into work. If, however, we introduce the quantity " entropy " we may say that the entropy passes through the cycle unchanged in

FIG. 230.   SMALL REVERSIBLE
                        CYCLES

amount, so that in a sense " entropy " replaces the earlier conception of " caloric ".*

Change of entropy in any reversible cycle. We now turn to the general case of any reversible cycle. Let any reversible transformation from the state A to the state B be represented by the curve AB on the indicator diagram (Fig. 230). We fix attention on any infinitesimal change PQ.

As it is reversible it may be regarded as equivalent to an isothermal change PR together with an adiabatic change RQ

Each infinitesimal element of the finite change AB may be treated in the same way, so that the whole change may be built up of a series of infinitesimal isothermal and adiabatic changes, as represented by the zigzag line joining A and B. It follows that any reversible cycle, represented on the indicator diagram by a closed curve, may be divided up into an infinite number of Carnot's cycles. This method was suggested by Clausius.

To construct such cycles we draw a series of adiabatics close together, and then introduce short isothermals (Fig. 231). Each resulting Carnot cycle is bounded by two adiabatics and two iso-

FIG. 231.   REVERSIBLE CYCLE BROKEN
UP INTO A LARGE NUMBER OF SMALL
CARNOT CYCLES

thermals. For each such Carnot cycle the previous relation holds and may be written in the form

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0.$$

* This way of regarding " caloric " was described and emphasised by Professor H. L. Callendar in his presidential address to the Physical Society in 1911.

Taking the sum of these results for all the cycles we conclude that for the finite cycle represented by the closed curve, $\sum \dfrac{\delta Q}{T}$ must be zero, or $\int \dfrac{dQ}{T} = 0$. This integral refers to the complete cycle, and in modern notation the fact that this is a cyclic integral is represented by writing the integral sign thus: $\oint$. For any reversible cyclic transformation

$$\oint \frac{dQ}{T} = 0.$$

This result may be regarded as one way—and a most important way—of expressing the second law of thermodynamics. It has been derived by assuming the truth of the second law as previously given (p. 603), and conversely, if we assume this result to be true, we can deduce the second law as stated by Clausius or by Kelvin. In words, the formula may be expressed by saying that **in a reversible cycle the nett increase of entropy is zero.**

In the operations which constitute a Carnot cycle changes of Q and of T occur separately. According to Kelvin, the result stated above is true in general when the changes take place together. This is implied in the procedure, due to Clausius, in which we replace the change PQ by the equivalent changes PR and RQ. Now take any two states A and B on the indicator diagram (Fig. 232) and suppose that there is a reversible path of change by which we can pass from the state A to the state B. Then the value of $\int_A^B \dfrac{dQ}{T}$ measures the difference between the entropies of the system in these two states, for in symbols

$$\int_A^B \frac{dQ}{T} = \int_A^B dS = S_B - S_A.$$

Considering only reversible changes, the value of $\int_A^B \dfrac{dQ}{T}$ depends solely on the initial and final states, and is independent of the actual path by which transference is brought about. If then, ACB and ADB (Fig. 232) are such reversible paths, the entropy change along the path ACB is the same as the entropy change along the path ADB. Now suppose, starting from A, we carry the working substance through a complete cycle $ACBDA$. Then the increase of entropy along ACB is equal to the decrease of entropy along BDA, and the total change of entropy in the cycle is zero. We notice that in all reversible *adiabatic* changes

FIG. 232. REVERSIBLE CYCLE

the entropy remains constant, because in such changes there is no transfer-ence of heat to or from the working substance. Such changes may be called **isentropic,** or changes in which the entropy remains constant. It must be emphasised that this holds good only for reversible changes. *A reversible adiabatic is also an isentropic.*

MEASUREMENT OF ENTROPY

We have seen that for an infinitesimal reversible change the increase of entropy is defined as $dS = dQ/T$, and for a finite reversible change from a certain state A to another state B the increase of entropy is given by

$$S_B - S_A = \int_A^B dS = \int_A^B \frac{dQ}{T} .$$

Entropy is a property associated with a certain definite state, and it may be measured from some arbitrary zero corresponding to a particular state. Let A be chosen as a standard state, defined, say, by certain arbitrary values for p and v, and let us call the entropy of this state zero. Then the entropy for state B is given as $S_B = \int_A^B \frac{dQ}{T}$, because we have chosen S_A arbitrarily as zero.

In evaluating this integral we may choose *any* reversible path from A to B (Fig. 233). There are two particular cases of special interest :
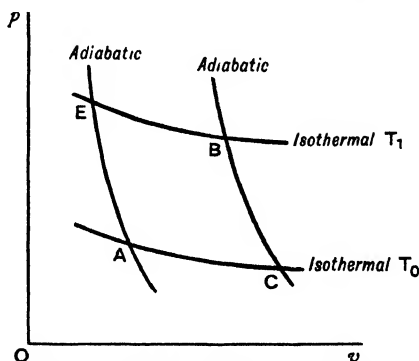
FIG. 233.   MEASUREMENT OF ENTROPY

(1) Let us select an isothermal AC passing through A, and an adiabatic BC passing through B, these curves intersecting in the point C. Then in the isothermal change AC the increase of entropy is Q_0/T_0, if we call the temperature of this isothermal T_0, and Q_0 the quantity of heat transferred along AC. In the adiabatic change CB the entropy remains constant ; there is no change in entropy. Hence $S_B = Q_0/T_0$. (2) We may select an adiabatic through A and an isothermal through B, these curves

intersecting in the point E. In the adiabatic change AE there is no change in entropy, whilst in the isothermal change EB the change in entropy is Q_1/T_1. Consequently S_B, the entropy of state B is equal to Q_1/T_1, where Q_1 is the quantity of heat imparted in the isothermal change EB at temperature T_1.

The two results are consistent, since $Q_1/T_1 = Q_0/T_0$.

Entropy is thus a definite physical property of a substance and depends *only* on the physical state of the substance, not on the process by which the substance has reached that state. In this respect it resembles the temperature or pressure of the substance, or the intrinsic energy it possesses. It is, in fact, possible to regard temperature and entropy as two quantities which are fundamental, just as, in earlier discussions, we regarded pressure and volume as fundamental. When this standpoint is taken we need not attempt to define temperature and entropy in terms of " simpler " quantities, for they themselves are regarded as simple and as equally fundamental, so that we do not then attempt to define one in terms of the other (Guggenheim).

The entropy temperature diagram. Willard Gibbs introduced a very convenient method of representing changes in entropy. The state of a substance, instead of being defined by the variables p and v, may be defined in terms of its entropy S and its temperature T, or, as some writers express it, in terms of ϕ and θ.

We construct a diagram (Fig. 234) in which temperatures are plotted parallel to the axis of Y, and the entropy plotted parallel to the axis of X.
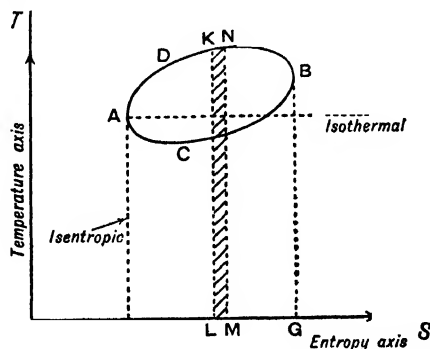
FIG. 234. ENTROPY-TEMPERATURE DIAGRAM

This we call the **entropy-temperature diagram.** The state of a substance may be represented by a point A having coordinates S and T. The isothermals are lines parallel to the axis of entropy ; the isentropics, or adiabatics, are lines parallel to the axis of temperature. Let A and B represent two states of a substance, and let the substance pass from one

20

state to the other by the reversible path ADB. Now $dS = dQ/T$, or $dQ = dS \times T$. If then, we take an infinitesimal change in entropy corresponding to $dS = LM$, the small amount of heat dQ is represented by the elementary shaded area $LMNK$. Consequently, the heat *taken in* during the change from A to B which is equal to $\int dQ$ is $\Sigma LMNK$, that is the area $ADBGH$, or the area under the curve ADB. Now take a reversible path BCA from B to A. It may be shown in the same way that the heat *given out* in this path is equal to the area $BCAHG$, that is the area under the curve ACB. In the cycle $ADBCA$ the net amount of heat taken in is equal to the difference between these areas, that is, it is equal to the area $ADBCA$.

The fundamental heat equation may be written $dQ = dU + dA$. At the end of a cycle, U, the intrinsic energy, is unchanged. Consequently the change in Q is equal to the change in A, which is the work done. Hence the work done in this reversible cycle is equal to the heat taken in, and is also represented by the area of the cycle on the diagram.

Let us now consider a particular case of such a reversible cycle, namely a Carnot cycle. This is shown in Fig. 235 (*a*) and (*b*). This cycle is
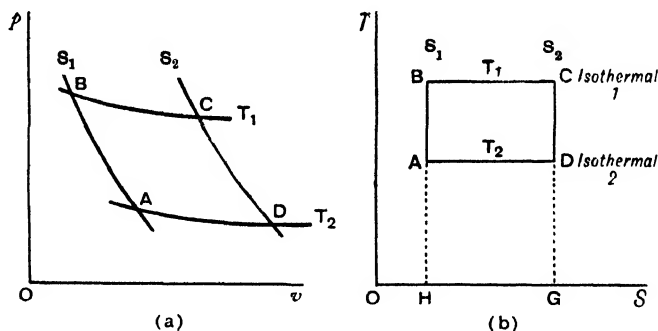
FIG. 235. CARNOT'S CYCLE (*a*) ON A p-v DIAGRAM, (*b*) ON AN S-T DIAGRAM

composed of two adiabatics and two isothermals and is represented by $ABCD$. In the adiabatic change AB the entropy remains constant; in the isothermal change BC the change in entropy is equal to Q_1/T_1, and this change may be called $S_2 - S_1$. From C to D there is no change in entropy; from D to A the change in entropy is equal to Q_2/T_2, or $S_2 - S_1$. Consequently we have $Q_1 = T_1(S_2 - S_1)$ and $Q_2 = T_2(S_2 - S_1)$. The quantity of heat Q_1 is represented by the area $BCGH$, and the quantity of heat Q_2 is represented by the area $ADGH$. Their difference $Q_1 - Q_2$ is represented by the difference between these areas, which is the area $ABCD$. In this case, then, the mode of representation is extremely

simple. This graphical method has been employed with success in the study of the steam engine.

We noticed on p. 616 that the p-v diagram could be divided into a number of equal areas by suitably drawing a series of isothermal and adiabatic curves. This result appears in a very simple form on the entropy-temperature (S-T) diagram (Fig. 236), for when entropy is
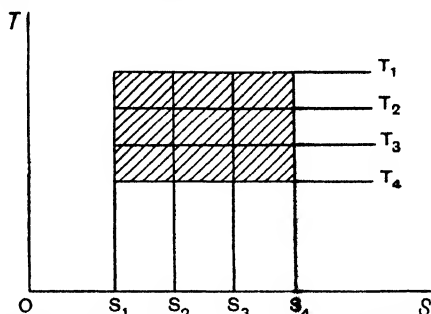
FIG. 236. ENTROPY-TEMPERATURE DIAGRAM CONTAINING RECTANGLES
OF EQUAL AREAS

taken as abscissa and temperature as ordinate the curvilinear quadrilaterals become rectangles. This may suggest the possibility of an absolute zero of entropy analogous to the absolute zero of the thermodynamic scale of temperature. This question will be taken up in a later chapter, when we shall see that, subject to certain restrictions, there is some justification for the idea.

Entropy of a perfect gas. We wish to find the **change of entropy** when a definite quantity (e.g. one mole) of a perfect gas passes from a state A to a state B. The fundamental equation expressing the first law may be written

$$dQ = C_v dT + p\, dv.$$

By definition,
$$S_B - S_A = \int_A^B \frac{dQ}{T}$$
$$= \int_A^B C_v \frac{dT}{T} + \int_A^B \frac{p\, dv}{T}$$
$$= C_v \int_A^B \frac{dT}{T} + \int_A^B R \frac{dv}{v} \quad (\text{since } pv = RT).$$
$$= C_v \log_e \frac{T_B}{T_A} + R \log_e \frac{v_B}{v_A}.$$

When the gas has traversed a *closed* cycle, B coincides with A and

$$S_B - S_A = C_v \log_e 1 + R \log_e 1 = 0,$$

thus verifying the result that the entropy change is zero.

We may, if we please, choose the state A as a *standard* state. Then the entropy in any other state may be written

$$S = C_v \log_e T + R \log_e v + \text{constant},$$

where the constant depends on the particular state chosen as standard.

PRINCIPLE OF INCREASE OF ENTROPY OR DEGRADATION OF ENERGY

The first law of thermodynamics implies, according to Clausius, that " the energy of the world remains constant "; the second law was summed up by him in the statement : " the entropy of the world tends to a maximum ".[*]

This principle of the tendency of entropy to increase is equivalent to Kelvin's statement that the " available energy " of the universe is tending towards zero. These principles we must now examine in detail.

Both statements stand in intimate relation to the distinction, previously discussed (p. 602), between reversible and irreversible processes. For although, as we have seen, the entropy of a system remains constant in reversible cyclic processes, in all irreversible processes the entropy of a system inevitably increases.

Reversible and irreversible processes. We have been considering for the most part *reversible* changes.

" Inasmuch as the conditions of reversibility are external conditions, any series of changes of temperature, pressure and volume in a body can be imagined to be carried out reversibly by suitably adjusting the external surroundings." [†]

It has, however, been said that " a reversible process is, strictly speaking, an impossibility ".

These apparently contradictory statements may be reconciled if it is remembered that a reversible process represents a limiting ideal case, and all actual processes in physics are irreversible. There has been considerable discussion as regards vital processes, but leaving these aside we may assert : The actual changes which occur in Nature are not reversible. It is necessary, then, to consider carefully actual or irreversible processes. Every system, left to itself, changes in such a way as to approach a state of rest, or of statistical equilibrium. A system will not change in the opposite direction, that is, away from the state of equilibrium, except through the influence of external agencies. This statement as to natural processes expresses the general experience of

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[*] " Die Energie der Welt ist konstant, die Entropie der Welt strebt einem Maximumzu ".

[†] Poynting and Thomson, *Heat*, p. 274, footnote.

mankind with regard to matter in bulk. There may be exceptions in dealing with atomic or molecular phenomena, as in the case imagined by Clerk Maxwell, and discussed below.

Maxwell's demon. In this imaginary experiment, a vessel is divided into two compartments by a partition with a small opening (Fig. 237). The aperture is fitted with a door under the control of an infinitesimal being, called by Maxwell a demon, who can open or shut the door at will. He is supposed to watch the approaching molecules and to allow only certain individual molecules to pass through the opening. For example, he might allow only the more rapidly moving molecules to pass. In

FIG. 237. MAXWELL'S DEMON

this way the temperature of one compartment would be raised; the temperature in the other lowered. Such a demon could reverse processes which to man alone are irreversible.
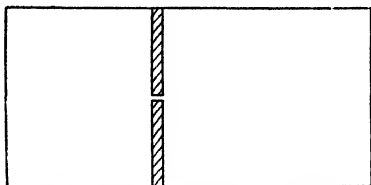
Natural processes are alike in one respect, in that they are bringing the various systems towards the condition of ultimate equilibrium or rest, and we may think of these systems as thereby losing in some measure their capacity for spontaneous change.

Dissipation of energy. The first law of thermodynamics asserts the conservation of energy. The second law is sometimes called the law of dissipation or degradation of energy. This implies not any loss in energy, but rather a loss in the availability of energy for external purposes. There is a degradation of the system as a whole, rather than a degradation of energy. For instance, in the diffusion of one gas into another the process does not essentially involve an energy change. Any actual process is said to be irreversible, because it is impossible to invent a means of restoring every system to its original condition. A reversible process is an ideal process, in which all sources of dissipation are eliminated. It may be regarded as *a limit* of an actually realisable process. The principle of the degradation of energy may be stated in terms of entropy.

According to Clausius the entropy of any self-contained system always tends to increase to a maximum value. It must be remembered that the definition of entropy involves the consideration of a reversible transformation from one state to another. If, then, a system passes from a state A to a state B by any reversible process, the increase of entropy is $\varSigma \delta Q/T$, the sum being taken for any reversible process by which the system can pass from the first state to the second.

Suppose the system consists of only two bodies, a warm body (1), and a cold body (2), the first being at temperature T_1 and the second at

temperature T_2, the difference between these temperatures being *finite*. Let a quantity of heat δQ be transferred from the hot body to the cold body by a reversible process, say by a heat engine. Then the first body loses an amount of entropy $\delta Q/T_1$; the second body gains an amount of entropy $\delta Q/T_2$. If we consider the two bodies as forming one system, the system as a whole gains entropy, and the gain in entropy of the system is equal to

$$\frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} = \delta Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \delta Q\,\frac{T_1 - T_2}{T_1 T_2}.$$

Since T_1 is, by hypothesis, greater than T_2, this is a positive quantity. Consequently the entropy of the system is increased by the passage of heat from the hot body to the cold body.

Now suppose the transference of heat takes place by conduction. This is an irreversible process, but the change of entropy is still given by the same expression, and consequently the system as a whole gains entropy. According to Clausius this result is true in general. For all actual processes the change which takes place corresponds to an increase in the entropy of the system.

Let us next consider a system consisting of a source at T_1, a sink at T_2, and a working substance that passes through a complete cycle of operations. In a *reversible* cycle the entropy is unchanged (p. 623).

When an element of *irreversibility* is present at any stage in a Carnot cycle, the efficiency is lowered. This means that instead of having

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}, \quad \text{we shall have} \quad \frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1},$$

since the actual efficiency $\dfrac{Q_1 - Q_2}{Q_1}$ will be less than the ideal value $\dfrac{T_1 - T_2}{T_1}$.

Hence
$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1};$$
$$-\frac{Q_2}{Q_1} < -\frac{T_2}{T_1};$$
$$\frac{T_2}{T_1} - \frac{Q_2}{Q_1} < 0;$$
$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0.$$

Finally
$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0.$$

Consequently, as it is assumed that the working substance has returned to its initial state at the end of the cycle, the entropy of the system *taken as a whole* increases.

Available energy. We have seen that according to Clausius the entropy of a self-contained system tends towards a maximum. Another way of expressing this result is given by Kelvin who introduced what he called the *available energy* of a system. Let us consider a simple Carnot cycle (see Fig. 235).

Taking two isothermals at temperatures T_1 and T_2 respectively, and supposing Q_1 to be the amount of heat received from the source at the higher temperature, Q_2 the amount of heat given to the sink at the lower temperature, we know that $Q_1/T_1 = Q_2/T_2$. The efficiency ϵ is $\dfrac{Q_1 - Q_2}{Q_1}$, or $\dfrac{T_1 - T_2}{T_1}$. Hence we may write: $Q_1 - Q_2 = \epsilon Q_1$. This represents that part of the heat derived from the source which is converted into work in the cycle. Since $\epsilon = \dfrac{T_1 - T_2}{T_1}$, we have $Q_1 - Q_2 = \dfrac{T_1 - T_2}{T_1} \times Q_1$, a result which follows directly from the fact that $Q_1/Q_2 = T_1/T_2$.

Kelvin then introduces into the discussion the *coldest body of any given system*. Let us call the temperature of this body T_0. By using this cold body, the amount of heat which can be converted into work is $\dfrac{T_1 - T_0}{T_1} \times Q_1$. Kelvin called this quantity the **available energy**, or **motivity**. The value of the available energy depends on the temperature of the coldest body available. The lower the temperature T_0, the greater is the available energy. For example, the available energy would be greater when liquid air is available than it is when only ice is available. If the absolute zero of temperature were available we should have $T_0 = 0$, and the available energy would be Q_1. That is, the whole quantity of heat Q_1 would be converted into work.

Corresponding to the principle of Clausius as to increase in entropy, Kelvin enunciated the principle : **The available energy of the universe is tending towards zero.** This statement may be illustrated by considering the transference of heat from a hot body to a cold body. Suppose a quantity of heat Q is transferred from a body at temperature T_1 to another body at temperature T_2. Then, as we shall see, there is a loss of available energy. Let T_0 be the lowest available temperature. Then the available energy to start with is $\dfrac{T_1 - T_0}{T_1} \times Q$. When the heat Q is given to the body at the temperature T_2 the *loss* of available energy is equal to

$$\frac{T_1 - T_0}{T_1} \times Q - \frac{T_2 - T_0}{T_2} \times Q = \left(1 - \frac{T_0}{T_1}\right)Q - \left(1 - \frac{T_0}{T_2}\right)Q = Q T_0 \left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Since T_2 is less than T_1 this quantity is positive, so that the available energy tends to diminish. The *loss* of available energy or the *increase* of

unavailable energy is equal to $T_0 \left(\dfrac{Q}{T_2} - \dfrac{Q}{T_1} \right)$, that is, $T_0 \times$ (the increase in entropy). This provides an alternative definition of entropy, namely, that the increase of entropy of a substance multiplied by any low temperature gives the increase of unavailable energy of the substance with reference to that temperature. The statements here given illustrate very general results.

WORKED EXAMPLES

1. *Find the difference of entropy of 1 gram of water at 0° C. and 1 gram of saturated steam at 50° C. at 1 atmosphere if* $L_{50} = 571 \cdot 7$ *calories per gram.*

For the water state, remembering that the absolute temperatures are 273° K. and 323° K. respectively, and assuming the specific heat of water to be unity,

the change in entropy $= \log_e (323/273) = (\log_{10} 323 - \log_{10} 273) \times \log_e 10$

$$= (2 \cdot 5092 - 2 \cdot 4362) \times 2 \cdot 3026$$

$$= 0 \cdot 168 \text{ calorie per degree C.}$$

For vaporisation,

change in entropy $= \dfrac{571 \cdot 7}{323} = 1 \cdot 77$ calories per degree C. ;

∴ total change in entropy $= S_B - S_A = 1 \cdot 938$ calories per degree C.

2. *Calculate the change of entropy when one gram atom of solid mercury at its melting point is raised to a temperature of 40° C.* [*Melting point of mercury* $= -39°$ *C. ; latent heat of fusion* $= 3$ *cal./gm. : mean specific heat over the required range of temperature* $= 0 \cdot 0335$ *cal. gm.*$^{-1}$ *°C.*$^{-1}$.]

One gram atom of mercury is 200 grams.

(1) Melting point $= -39°$ C. This is $(273 - 39) = 234°$ K.
Latent heat of fusion $= 3$ cal. per gm.
Melting takes place at constant temperature.

$$S_B - S_A = \frac{Q}{T} = \frac{200 \times 3 \text{ cal.}}{234°} = 2 \cdot 565 \text{ cal. per degree C.}$$

(2) Temperature raised to 40° C. or 313° K.

$\delta Q = mc \, dT$ where $c = 0 \cdot 0335$ is assumed constant.

$$S_B - S_A = \int_A^B \frac{mc \, dT}{T} = mc \left[\log_e T \right]_A^B$$

$$= mc \left[\log_{10} 313 - \log_{10} 234 \right] \log_e 10$$

$$= 200 \times 0 \cdot 0335 \times 0 \cdot 1263 \times 2 \cdot 303$$

$$= 1 \cdot 949 \text{ cal. per degree C.}$$

Total change in entropy $= 2 \cdot 565 + 1 \cdot 949 = 4 \cdot 514$ calories per degree C.

QUESTIONS

CHAPTER XXX

1. Define *entropy* and show how to calculate the excess of entropy of unit mass of (*a*) water, (*b*) saturated steam, at $t°$ C. above that of unit mass of water at $0°$ C.

Sketch the temperature-entropy diagram for water and saturated steam and show how it indicates that the specific heat of saturated steam is negative. Explain the meaning of a negative specific heat.   (L.U., B.Sc.)

2. Define the entropy of a substance, and show that if the entropy of a pure substance at the absolute zero of temperature is zero, then its specific heat and its temperature coefficient of volume expansion must also be zero.   (L.U., B.Sc.)

3. Explain the meaning of the term *entropy* as applied to a gas or any system whose equation of state is a relation between P, V and T. Derive an expression for the increase in the entropy of an ideal gas when it is allowed to expand adiabatically into a previously exhausted space.   (L.U., B.Sc.)

4. Explain what is meant by the entropy of a substance. Calculate the change in entropy when 5 gm. water at $0°$ C. are raised to $100°$ C. and converted into steam at that temperature. Latent heat of steam at $100°$ is 539 calories/gm.

5. Explain the meaning of the term entropy.
Calculate the change in entropy when one gram atom of solid mercury is melted and then has its temperature raised to $15°$ C.
[Data for mercury: latent heat of fusion, 3 cals./gm ; specific heat of liquid (assumed constant), 0·034 ; atomic weight, 200·6 ; melting point, $-39°$ C.]
                                                                     (St. A. U.)

6. Explain clearly what is meant by the term entropy.
Calculate the change in entropy when 23 gm. of sodium is heated from $0°$ C. to its melting point, $98°$ C., assuming that the specific heat remains constant and equal to 0·3 cal. gm.$^{-1}$ deg.$^{-1}$.   (St. A. U.)

7. Explain the meaning of the term " entropy ".
The melting point of tin is $232°$ C., the latent heat of fusion is 14 calories per gram, and the specific heat of solid and molten tin 0·055 and 0·064 respectively. Calculate the change of entropy when 1 gm. of tin is heated from $150°$ C. to $314°$ C.
                                                            (E.U. Inter. Hons.)

8. Find the change in entropy for the following substances on being vaporised at the boiling point, given the heat equivalent per mole :

				Boiling point	Heat equivalent in cal. per mole
Ether -	-	-	-	$307·7°$ K.	6500
Benzene	-	-	-	$353·3°$ K.	7353
Chlorbenzene	-	-	-	$405·1°$ K.	8730
Chloroform	-	-	-	$334·4°$ K.	6925
Toluene	-	-	-	$384·0°$ K.	7736

9. Find the change in entropy when one mole of benzene (C_6H_6) changes state from the following (approximate) data :
Formula weight, 78 ; melting point, $5·5°$ C. ; latent heat, 30 cal./gm.

10. Discuss entropy-temperature diagrams.
Show that the entropy of a system of two bodies is increased by conduction taking place in it.   (E.U. Inter. Hons.

THERMODYNAMICS OF CHANGE OF STATE

It is well known that a substance in general can exist either as a solid, a liquid, or a gas, and under suitable conditions certain of these states may exist together in equilibrium. Thus when a solid is in equilibrium with its own liquid, we call the temperature the melting point, and, as we have seen, the value of the melting point depends on the pressure at which the experiment is carried out. Again, we may have a saturated vapour in equilibrium in contact with its own liquid, and according to the law of Dalton, the pressure is independent of the relative proportions of liquid and vapour, and depends only on the temperature. The form of the isothermal curve in this case is clearly shown in the experiments of Andrews on carbon dioxide (Fig. 238).

FIG. 238. ISOTHERMALS OF CARBON DIOXIDE

$OM = v_2$, $ON = v_1$, $BC = NM = v_2 - v_1$

The isothermal consists of three parts, AB, BC, CD; the first part AB corresponding to the liquid stage, the horizontal part BC to the saturated vapour in contact with its own liquid, and CD to the unsaturated vapour. We may suppose the substance contained in a cylinder with its axis parallel to the axis of v. Starting with the unsaturated vapour and diminishing the volume, the pressure increases approximately in accordance with Boyle's law until a volume $OM = v_2$ is reached. At the point C condensation is just about to begin. As the piston is pushed further in, condensation takes place, but the pressure remains constant until a volume $ON = v_1$ is reached corresponding to the point B on the isothermal, at which stage the whole of the vapour is reduced to the liquid state. At some lower temperature, $T - dT$, the isothermal is represented by $A'B'C'D'$. Points such as BB', CC' may be joined by a curve, shown dotted, which divides the indicator diagram into two regions.

THE FIRST LATENT HEAT EQUATION

Vaporisation. We may apply Carnot's theorem to obtain the relation between the latent heat of evaporation and the rate of change of pressure

634

with temperature. The Carnot cycle (Fig. 239) includes two isothermal changes and two adiabatic changes. Let $\alpha\beta\gamma\delta$ be such a cycle composed of the two adiabatics $\alpha\beta$ and $\gamma\delta$, and two isothermals $\beta\gamma$ and $\alpha\delta$, corresponding to temperatures T and $T - dT$. Starting from the point α, the cylinder containing the substance is placed on the non-conducting stand and an adiabatic compression takes place, while the temperature changes from $T - dT$ to T. The cylinder is then placed on the source at temperature T,

FIG. 239. CARNOT CYCLE FOR
SATURATED VAPOUR

and the substance is allowed to expand isothermally a change in volume represented by $\beta\gamma$ taking place. The cylinder is then put back on the non-conducting stand and an adiabatic expansion takes place, while the temperature falls from T to $T - dT$, the change being represented by $\gamma\delta$. Finally the cylinder is transferred to the cold reservoir, and compression takes place at constant temperature until the initial state is reached. The cycle is reversible, for it could have been described in the direction $\alpha\delta\gamma\beta\alpha$.

We require the area of the figure $\alpha\beta\gamma\delta$. For our present purpose it is not necessary to know the exact form of the adiabatic curves $\alpha\beta$ and $\gamma\delta$. If β and γ are close together, the curve $\alpha\beta$ will be approximately parallel to the curve $\delta\gamma$. Consequently the area of the cycle $\alpha\beta\gamma\delta$ will be equal to $\beta\gamma \times dp$, where dp is the small pressure difference corresponding to the small temperature difference dT.

Now let Q represent the heat taken in from the source along $\beta\gamma$, Q' the heat given out along $\delta\alpha$. Then, as we are using the thermodynamic scale for T, we have

$$\frac{Q}{T} = \frac{Q'}{T'} = \frac{Q - Q'}{T - T'} = \frac{Q - Q'}{dT},$$

where $T - dT$ is represented by T'. Q corresponds to the heat required to vaporise a certain mass of substance at the higher temperature. Let the mass of liquid vaporised between β and γ be m. Then $Q = mL$ where L is the latent heat of vaporisation for unit mass. $Q - Q'$ is equal to the external work in the cycle, i.e. the area of the cycle $\alpha\beta\gamma\delta$. Thus $Q - Q' = \beta\gamma \times dp$. Let v_1 and v_2 be the specific volumes, i.e. volumes referred to unit mass. Then

$$\beta\gamma/BC = m/1, \quad \text{or} \quad \beta\gamma = m(v_2 - v_1),$$

so that $\qquad\qquad Q - Q' = m(v_2 - v_1)\,dp.$

Substituting these values in the equation

$$\frac{Q}{T} = \frac{Q - Q'}{dT},$$

we get

$$\frac{mL}{T} = \frac{m(v_2 - v_1) \, dp}{dT}.$$

The mass m occurs on both sides of the equation and cancels, and we obtain what is called the **first latent heat equation.**

$$\frac{L}{T} = (v_2 - v_1) \frac{dp}{dT}.$$

This important equation is named after Clapeyron (1834) and Clausius (1850). It was also obtained by Sir William Thomson (1850). It should be noticed that in the limit, when dp/dT represents a differential coefficient, this equation is exact.

The quantity L/T in the first latent heat equation represents the change of entropy corresponding to the change of state that takes place at constant temperature. Calling this change of entropy $S_2 - S_1$, we have

$$S_2 - S_1 = (v_2 - v_1) \frac{dp}{dT} \quad \text{or} \quad \frac{S_2 - S_1}{v_2 - v_1} = \frac{dp}{dT}.$$

In deriving the first latent heat equation we have been considering unit mass of substance, and the symbols L, S and v have been defined with reference to unit mass. This unit mass may be chosen at will as, for example, 1 gram or 1 mole. But in using the equation it is necessary to be consistent. Thus if L is the molecular latent heat in calories per mole and S is the entropy per mole, v is the specific volume in c.c. per mole. If L is in calories per gm. and S is the entropy per gm., v is in c.c. per gm. Some writers use l and s in this latter case.

Applications of the first latent heat equation.

1. CALCULATION OF THE LATENT HEAT. The equation may be applied in several different ways. We may, for example, use it in calculating the latent heat of evaporation of water at 100° C., assuming the other quantities in the equation known. We write the equation in the form

$$L = T(v_2 - v_1) \, dp/dT.$$

$T = 273 + 100 = 373°$ K. ; $dp/dT = 27 \cdot 12$ mm. of Hg per 1° C. at 100° C.

There is some uncertainty as to the value to be assigned to v_2 (the specific volume of saturated vapour). We shall assume a value, which is due to Knoblauch, Linde and Klebe, of $v_2 = 1674$ c.c. We know that for water $v_1 = 1$ c.c. ; therefore $v_2 - v_1 = 1673$ c.c. We notice further that the right-hand side of the equation is measured in work units (ergs) ;

if we desire to measure the latent heat in heat units, it is necessary to divide the right-hand side by J. We shall assume a value

$$J = 4 \cdot 18 \times 10^7 \text{ ergs/calorie.}$$

The calculated value of the latent heat then becomes

$$L = \frac{373 \times 1673 \times 2 \cdot 712 \times 13 \cdot 6 \times 981}{4 \cdot 18 \times 10^7} = 539 \cdot 7 \text{ calories per gram.}$$

2. CALCULATION OF THE SPECIFIC VOLUME. It might be more reasonable to reverse the order of the calculation and use the formula for finding v_2, which is a quantity rather difficult to determine experimentally.

The values of L found by experiment are as follows :

Dieterici (1905)	$L = 538 \cdot 9$ calories per gram.
Henning (1906)	$L = 539 \cdot 6$ calories per gram.
Smith (1911)	$L = 540 \cdot 5$ calories per gram.
Richards and Mathews (1911)	$L = 538 \cdot 0$ calories per gram.

Assuming as a mean value $L = 539 \cdot 2$ calories per gram, the value of $v_2 - v_1$ is found to be 1671 c.c.

3. CALCULATION OF THE ALTERATION OF THE BOILING POINT WITH PRESSURE. Alternatively we may employ the Clapeyron-Clausius equation to determine the depression of the boiling point produced by a given diminution of pressure. This means that we write the equation in the form

$$dT = \frac{T(v_2 - v_1)}{L} dp,$$

and calculate dT for an assigned value of dp. If, for example, we put dp equal to 1 mm. of mercury, or $0 \cdot 1 \times 13 \cdot 6 \times 981$ dynes per sq. cm., we find approximately for water $dT = 0 \cdot 036°$ C.

Fusion. For any assigned pressure p there is a definite melting point T in the case of a pure crystalline solid, so that p is some function of T.

The same thermodynamic method may be employed to calculate the alteration in the melting point of a substance produced by a given increase of pressure. The process is exactly the same as that already described, but L now represents the latent heat of fusion of the solid, v_1 the volume occupied by one gram of the solid, v_2 the volume occupied by one gram of the liquid.* The equation obtained is, as before, the Clapeyron-Clausius equation, $\qquad L = T(v_2 - v_1) dp/dT.$

In this case, however, we wish to determine the change in the melting point, dT, corresponding to a certain change in the pressure dp. For this purpose the equation may be written

$$dT = T \frac{(v_2 - v_1)}{L} \times dp.$$

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* It should be noticed that in the previous discussion, dealing with vaporisation, the specific volume of the *liquid* was called v_1.

The difference between v_1 and v_2 is very small, and the quantity $v_2 - v_1$ may be either positive or negative. Two cases arise : (1) The quantity $v_2 - v_1$ is positive, or the substance expands on melting. Examples are paraffin wax or sulphur. We may describe such substances as of the wax or sulphur type. (2) Some substances behave in the opposite way. In this case contraction occurs on melting and $v_2 - v_1$ is negative. Water-ice is the best known example of this kind.

Numerical examples. We shall now consider two numerical problems, one of the wax type and the other of the ice type.

(1) Edser takes paraffin wax as an example. The latent heat of fusion, L, he gives as 35·35 calories per gram, the increase in volume of one gram on melting as $v_2 - v_1 = 0·125$ c.c. and the melting point T, under ordinary pressure as 52·7° C., that is, 52·7° + 273·2°, or 325·9° on the absolute scale. Now take dp as one atmosphere, or $dp = 1013000$ dynes per sq. cm.

Then
$$dT = \frac{325·9 \times 0·125 \times 1·013 \times 10^6}{35·35 \times 4·18 \times 10^7} = 0·028°\,\text{C}.$$

The melting point of paraffin wax should be *raised* by 0·028° C. when the pressure is *increased* by 1 atmosphere. The experiments of Batelli showed a rise of 0·03° C. in the melting point of paraffin wax when the pressure was increased by 1 atmosphere.

(2) Now let us consider the effect of pressure on the melting point of ice. The specific volumes found by experiment are : for water, $v_2 = 1·000116$ c.c. ; and for ice, $v_1 = 1·087$ c.c. ; therefore $v_2 - v_1 = -0·087$ c.c.

$$T = 273°\,\text{K.} \quad \text{and} \quad L = 80 \text{ calories per gram.}$$

Hence, for ice.
$$dT = \frac{273 \times (-0·087) \times 1·013 \times 10^6}{80 \times 4·18 \times 10^7} = -0·007°\,\text{C}.$$

Thus at zero pressure the melting point of ice would be raised above 0° C. to 0·007° C.

When the pressure is increased above atmospheric pressure the freezing point of water will be lowered by 0·007° C. for each additional atmosphere of pressure. Dewar experimented up to 700 atmospheres and found a depression of 0·0072° C. per atmosphere. Thus it appears that there is good agreement between theory and experiment.

Melting point of ice under various pressures. The effect produced on the melting point of ice by change of pressure is implied in the First Latent Heat Equation. As predicted by James Thomson, and verified by his brother William (Lord Kelvin), an increase of pressure is accompanied by a diminution of the melting point. This case is of such importance that we shall now investigate the theory from first principles.*

* We here follow the method given in Edser's *Heat for Advanced Students*, 1929 edition, p. 373.

The horizontal lines on the p-v diagram (Fig. 240) represent isothermals corresponding to the melting points of ice under two different pressures p and $p - dp$. The temperatures of the isothermal for pressure p we shall call T_1, and the temperature of the isothermal for pressure $p - dp$ we shall call T_2. Our object is to find whether the temperature T_1 is higher or lower than the temperature T_2.

Let us consider an ideal heat engine, the cylinder of which contains a mixture of water and ice, and suppose that the engine is carried through a Carnot cycle.
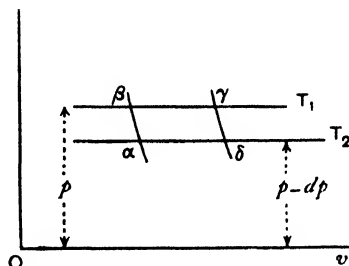
FIG. 240. MELTING OF ICE UNDER DIFFERENT PRESSURES

PROCESS 1. Starting with the contents in a condition represented by the point α on the diagram, the temperature being T_2, we suppose an adiabatic compression carried out, the temperature changing to T_1 and the condition being then represented by β.

PROCESS 2. This is an isothermal change at temperature T_1, the material expanding isothermally to the condition shown by γ. This means that a certain quantity of water must be converted into ice. Consequently a quantity of heat Q_1 must have been *given up* such that

$$Q_1 = \text{(mass of water frozen)} \times \text{(latent heat)}.$$

PROCESS 3. This is an adiabatic expansion from γ to δ accompanied by a change of temperature from T_1 to T_2.

PROCESS 4. An isothermal change at temperature T_2 accompanied by contraction. This means the conversion of ice into water, and therefore the *absorption* of a quantity of heat Q_2 at temperature T_2 given by

$$Q_2 = \text{(mass of ice melted)} \times \text{(latent heat)}.$$

The *external work* done is represented by the area $\alpha\beta\gamma\delta$, and this

$$= dp \times \beta\gamma.$$

This external work can only be performed when heat is *absorbed* at a high and *rejected* at a lower temperature.

This implies that T_2 is higher than T_1, in other words, the melting point under a pressure $p - dp$ is higher than the melting point under a pressure p. Thus the effect of an increase of pressure is to lower the melting point.

The triple point. In Chapter XI (p. 274) we discussed the equilibrium of a substance in its solid, liquid, and vapour states, and pointed out the

existence of a triple point in the case of a substance such as water. In such a condition the vapour pressures of the substance in each of the three states are identical. We are now in a position to calculate the slopes of the three curves which form the boundaries between the three states on the pT diagram (Fig. 119, p. 275). To do this, we make use of the First Latent Heat Equation which, for the present purpose, may be written in the form

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)} \cdot$$

The differential coefficient on the left-hand side of the equation represents the slope of the curve, and we can make three separate applications and so find the slope of each line under consideration.

(1) For the steam line, $\dfrac{dp}{dT} = \dfrac{L_{\text{vaporisation}}}{T(v_g - v_l)}$,

where v_g refers to the volume of the vapour, and v_l refers to the volume of the liquid.

For steam at 0°, we find the slope $= 0.337$ mm. of mercury per degree.

(2) For the hoar frost line,

$$\frac{dp}{dT} = \frac{L_{\text{sublimation}}}{T(v_g - v_s)},$$

where v_s refers to the volume in the solid state.

For water vapour, we find 0.376 mm. of mercury per degree.

Thus the slopes are not identical, and the two curves are not continuous as was at one time supposed.

(3) For the fusion line, $\dfrac{dp}{dT} = \dfrac{L_{\text{fusion}}}{T(v_l - v_s)} \cdot$

In this case we find, for water-ice,

$$\frac{dp}{dT} = \frac{80 \times 4.18 \times 10^7}{273(1 - 1.091)} = -1.3 \times 10^8 \text{ dynes per sq. cm. per degree.}$$

This is equivalent to -9.7×10^4 mm. of mercury per degree so that the curve is almost vertical.

The coordinates of the triple point on the pT diagram are $T = 0.0075°$ C., $p = 4.58$ mm. of mercury. At this point the three states, solid, liquid, and vapour, coexist.

The phase rule. The existence of the " triple point " serves to illustrate a principle of a general character, known as the **phase rule**, enunciated by Willard Gibbs (1878). The three states, solid, liquid, and vapour, of a pure substance represent three different " phases " of the substance, the term **phase** being used to denote a physically distinct portion of a system which is separated from other portions by a boundary surface.

According to the phase rule, the number of degrees of freedom of a system is given by

$$F = C - P + 2,$$

where C is the number of *components*, P the number of *phases*.

In the case of water at the triple point, there is only one component (water) but three phases (ice, water, steam) and the system should have *no* degree of freedom.

It is an experimental fact that there is a single definite temperature at which the three phases are in equilibrium, any change of temperature results in the disappearance of one phase. A similar remark is true as regards pressure. The system is said to be *non-variant*, or to have no degree of freedom.

The Phase Rule has its more important applications in dealing with systems containing two or more components, as when a salt is dissolved in water, or when a freezing mixture is formed by mixing salt with ice. In addition to numerous applications in physical chemistry it is also of importance in metallurgy.*

THE SECOND LATENT HEAT EQUATION

In the first latent heat equation we are concerned with the latent heat L at a particular temperature T. The value of the latent heat is not a constant but depends upon the temperature.

For example, Henning found that the latent heat of steam between $30°$ and $100°$ C. could be expressed to an accuracy of 0.3 per cent. by the formula

$$L_t = 599.4 - 0.60t,$$

where t is the temperature in °C.

Thus for $\qquad t = 100°$ C., $\quad L_{100} = 599.4 - 60 = 539.4,$

but for $\qquad t = 90°$ C., $\quad L_{90} = 599.4 - 54 = 545.4,$

the results being expressed in calories per gram.

The second latent heat equation is concerned with this temperature variation. Clausius showed how to obtain this second equation connecting the latent heat and *its variation with temperature* with the specific heats of the substance in the two states.

To fix our ideas we may suppose that we are dealing with a liquid and its vapour so that L is the latent heat of vaporisation. This change from the state of liquid to that of vapour takes place at constant temperature T. Consequently L/T is the increase in entropy in passing from the liquid state to the state of vapour, that is

$$L/T = S_2 - S_1.$$

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* A. Findlay, *Phase Rule and its Applications*, Longmans, Green & Co., 1922.

Here S_2 refers to the entropy in the state of vapour, S_1 to that in the state of liquid. Differentiate this expression with regard to the temperature.

Then
$$\frac{d}{dT}\left(\frac{L}{T}\right) = \frac{dS_2}{dT} - \frac{dS_1}{dT},$$

or
$$\frac{1}{T}\frac{dL}{dT} - \frac{L}{T^2} = \frac{dS_2}{dT} - \frac{dS_1}{dT}.$$

Hence
$$\frac{dL}{dT} - \frac{L}{T} = \frac{T\,dS_2}{dT} - \frac{T\,dS_1}{dT}.$$

The two expressions which occur on the right-hand side of the equation may be interpreted as specific heats. For (remembering that $dS = dQ/T$), $T\,dS_2$ represents the heat taken in by the substance in the second state (vapour) when its temperature rises by an amount dT; consequently $T\,dS_2/dT$ may be treated as a specific heat (C_2 say). We may regard it as **the specific heat of the saturated vapour.** We have seen previously that there are any number of specific heats, the value depending on the conditions of the experiment. This is neither a specific heat at constant volume nor a specific heat at constant pressure, but it is a specific heat *subject to the condition that the vapour is kept just on the point of saturation.* Similarly, the expression $T\,dS_1/dT$ may be interpreted as a specific heat, and we may call it C_1, where C_1 is the **specific heat of the liquid at saturation pressure.**

The equation now takes the form

$$dL/dT - L/T = C_2 - C_1,$$

and this is known as the Equation of Clausius, or the **Second Latent Heat Equation.**

As explained on page 565 the unit of mass employed in defining C_1 and C_2 may be either the mole or the gram, according to the way in which L is defined.

Alternative derivation of the second latent heat equation. This equation may be deduced in a number of other ways. A very interesting method is given in Preston's *Theory of Heat,* in which the substance is taken round a cycle $B'BCC'B'$, where $ABCD$ and $A'B'C'D'$ are two neighbouring isothermal curves. This is not a Carnot cycle, because BB' and CC' are not adiabatics. They are, in fact, portions of the boundary curve separating the different regions of the indicator diagram (Fig. 238). Along the line BB' the substance is *all* in the liquid state, along the line CC' it is all in the state of vapour *just* on the point of condensation. In fact CC' is the boundary curve separating the region of saturated from the region of unsaturated vapour. Let unit mass of substance be carried through the cycle $B'BCC'$. In passing from

B' to B the quantity of heat *absorbed* $= C_1\,dT$, where C_1 is the specific heat of the liquid just on the point of vaporisation. (This will be practically the same for *the liquid* as the ordinary specific heat of the liquid.) Along BC the heat *absorbed* by unit mass $= L$. In passing from C to C' the quantity of heat *given out* $= C_2\,dT$, where C_2 is the specific heat of the saturated vapour. Along $C'B'$ the heat *given out* by unit mass $-L - \dfrac{dL}{dT}\,dT$. Hence the total quantity of heat *absorbed* in the cycle is

$$\delta Q = C_1\,dT + L - C_2\,dT - \left(L - \frac{dL}{dT}\,dT \right)$$

$$= C_1\,dT - C_2\,dT + \frac{dL}{dT}\,dT.$$

But
$$\delta Q = (v_2 - v_1)\,dp = \frac{L\,dT}{T}$$

from the *first* latent heat equation.

Hence
$$\frac{L\,dT}{T} = C_1\,dT - C_2\,dT + \frac{dL}{dT}\,dT,$$

$$\frac{dL}{dT} \cdot \frac{L}{T} = C_2 - C_1 \quad \text{(Equation of Clausius)}.$$

Derivation by means of the entropy-temperature diagram. A somewhat different way of deducing the equation is to employ the entropy-temperature diagram in which the temperature is plotted as the ordinate and the entropy as the abscissa (Fig. 241). On this diagram let us draw a line of equal pressure, $ABCD$ (an isopiestic). Along BC, which is parallel to the axis of entropy, the temperature is constant. Draw a second line of equal pressure $A'B'C'D'$, and join BB', CC'. Then take the substance round the cycle represented by $B'BCC'$. Along $B'B$ heat is given to the substance of amount $C_1\,dT$. The heat given along BC is the latent heat L. Along CC' the heat given is $-C_2\,dT$, and along $C'B'$ it is $-\left(L - \dfrac{dL}{dT}\,dT \right)$.
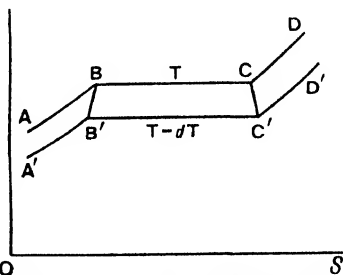
FIG. 241.   ENTROPY-TEMPERATURE DIAGRAM.   ISOPIESTICS

Adding all these together, the total heat given to the substance in the cycle is equal to

$$\frac{dL}{dT}\,dT + C_1\,dT - C_2\,dT.$$

This must be equal to the area of the cycle, $BCC'B'$, and we may treat the figure as being practically a rectangle and take the area as $BC \times dT$.

Now $BC \times T = L$, and therefore $BC = \dfrac{L}{T}$. Substituting the value $\dfrac{L}{T} dT$ for the area, we get

$$\frac{dL}{dT} dT + C_1 dT - C_2 dT = \frac{L}{T} dT.$$

Therefore

$$\frac{dL}{dT} + C_1 - C_2 = \frac{L}{T},$$

or

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1 \text{ (Equation of Clausius).}$$

Specific heat of saturated vapours. The second latent heat equation is of special interest because it gives us a method of calculating the specific heat of saturated vapour.

At the point C (Fig. 238) the substance is in the state of vapour at temperature T, and at the point C' it is still in the state of vapour but at temperature T'.

The dotted curve joining C and C' is the **curve of saturation.**

Consider the passage of unit mass of steam from the state represented by C' to that represented by C. It is possible for the steam to be *guided* along this path $C'C$ by suitable compression accompanied by the addition (or subtraction) of heat. This question is discussed very clearly in the *Thermodynamics* of Planck (§ 184). Let us start with the fundamental heat equation $dQ = dU + p\,dv$. Dividing each term by dT, and noticing that dQ/dT corresponds to a specific heat C, we find

$$C = \frac{dU}{dT} + p \frac{dv}{dT}.$$

This specific heat equation is quite general in form. As Planck remarks, " No offhand statement can be made with regard to the value of C. Even its sign must in the meantime remain uncertain. If, for example, we are dealing with a vapour which is kept just saturated during the rise of temperature, it must evidently be compressed while being heated, since the specific volume of the saturated vapour decreases as the temperature rises. This compression, however, generates heat, and the question is whether the latter is so considerable that it must be in part withdrawn by conduction, so as not to superheat the vapour ". In the case of steam the heat of compression is so large that it is necessary to withdraw heat to maintain saturation at the higher temperature. This means that **the specific heat of saturated steam is negative.**

Numerical Examples.

1. STEAM. In the equation $C_2 = C_1 + dL/dT - L/T$ we may take the value of C_1 as $1\cdot01$ cal. gm.$^{-1}$ deg.$^{-1}$. dL/dT is negative and is equal

to -0.64 cal. gm.$^{-1}$ deg.$^{-1}$. This last statement, being interpreted, means that the latent heat of steam diminishes as the temperature rises.

Now $\qquad$ $L = 539$ calories per gram, $T = 373°$ K.,

giving $\qquad$ $L/T = 1.44$ calories per gram per °C.

Therefore $\qquad$ $C_2 = 1.01 - 0.64 - 1.44 = -1.07$ cal. gm.$^{-1}$ deg.$^{-1}$.

The specific heat of saturated steam is negative and equal to 1.07 calories per gram per degree.

2. ETHER. Some vapours behave in the opposite way, and the specific heat for these is positive. Let us take ether vapour as an example.

We may determine the specific heat of saturated ether vapour at its normal boiling point $35°$ C., given

$\qquad C_1 = $ specific heat of liquid $= 0.529 + 0.000592t,$

$\qquad L = $ latent heat of vaporisation $= 94 - 0.079t - 0.00085t^2.$

It follows that $dL/dt = -0.079 - 0.00085 \times 2t.$

For $t = 35°$ C.,

$\qquad C_1 = 0.529 + 0.000592 \times 35 = 0.5497$ cal. gm.$^{-1}$ deg.$^{-1}$.

$\qquad L = 94 - 0.079 \times 35 - 0.00085 \times (35)^2 = 90.2$ cal. gm.$^{-1}$.

$\qquad \dfrac{L}{T} = \dfrac{90.2}{273 + 35} = 0.2929$ cal. gm.$^{-1}$ deg.$^{-1}$.

$\qquad dL/dT = -0.079 - 0.00085 \times 35 \times 2 = -0.1386$ cal. gm.$^{-1}$ deg.$^{-1}$.

Therefore

$\qquad C_2 = -0.1386 - 0.2929 + 0.5497 = +0.1182$ cal. gm.$^{-1}$ deg.$^{-1}$.

Thus we see that the specific heat of saturated ether vapour is positive.

Hirn's experiments on saturated vapours. In 1862 Hirn made some experiments on the sudden adiabatic expansion of saturated vapours, and verified the theoretical results discussed above. He took a long copper cylinder constructed with parallel plates of glass at each end so that an observer could look along its length. Steam from a boiler was generated under a pressure of 5 atmospheres, that is at a temperature of $152°$ C., and was passed through the cylinder until all the air and condensed water had been driven out and the walls had attained the temperature of the steam. The outlet from the cylinder and the connection to the boiler were then closed so that the cylinder was now filled with dry saturated steam at a pressure of 5 atmospheres. On looking through the cylinder it appeared quite clear. The exit tap was suddenly opened and consequently the pressure then fell very rapidly. A dense cloud formed within the cylinder and rendered it opaque to the observer. This effect, however, only lasted for a short while and the cloud quickly disappeared as the vapour now at atmospheric pressure and at $100°$ C. rapidly absorbed heat from the walls of the cylinder at $152°$ C. Thus we see that the specific heat of saturated steam is negative.

Further experiments were made on ether vapour in the same manner, but the condensation effect was not obtained. However, when the substance was suddenly compressed the cloud formed. This shows that the specific heat of saturated ether vapour is positive.

Relation between latent heat of vaporisation and boiling point. Despretz in 1823 advanced an empirical rule (often called Trouton's rule *), connecting the latent heat of vaporisation with the boiling point on the absolute scale. According to this rule, the molecular latent heat divided by this temperature is a constant for all normal or non-polar liquids. This implies that the change in entropy is the same for such substances when one mole is considered, and the boiling point at normal atmospheric pressure is employed. There is some theoretical justification for Trouton's rule, provided the boiling points may be regarded as " corresponding " temperatures. In many cases the boiling points under atmospheric pressure are about two-thirds of the critical temperatures.

For liquids with high boiling points the rule does not give good results, and more constant results may be obtained by employing, instead of the boiling points, temperatures at which the *concentration* of the vapour has the same value.

WORKED EXAMPLES

1. *Calculate the specific volume of the vapour of carbon tetrachloride at the boiling point from the following approximate data : Boiling point, 77° C. at 1 atmosphere. Latent heat, 46 calories per gram. Density of liquid, 1·6 gm. per c.c. dp/dT, 23 mm. of mercury per degree C.*   (St. A. U.)

We use the first latent heat equation, and write

$$L/T = (v_2 - v_1)dp/dT.$$

Inserting the numerical values, and remembering that

$$T = 77 + 273 = 350° \text{ K.},$$

we have $$\frac{46 \times 4 \cdot 185 \times 10^7}{350} = (v_2 - v_1) \, 2 \cdot 3 \times 13 \cdot 6 \times 981.$$

$$\therefore \; v_2 - v_1 = \frac{46 \times 4 \cdot 185 \times 10^7}{350 \times 2 \cdot 3 \times 13 \cdot 6 \times 981} = 179 \cdot 3 \text{ c.c./gm.}$$

But $$v_1 = \frac{1}{1 \cdot 6} = 0 \cdot 6 \text{ c.c./gm.,}$$

$$\therefore \; v_2 = 179 \cdot 9, \text{ say } 180 \text{ c.c./gm.}$$

2. *When naphthalene melts at 80° C. the increase in specific volume is 0·146 c.c. per gram. Assuming the latent heat of fusion to be 35·6 calories per gram, find the change in the melting point per atmosphere pressure.*

In this case $$T = 273 + 80 = 353° \text{ K.,}$$

and $dp = 1$ atmosphere $= 1,013,000$ dynes per sq. cm.

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* See Partington's *Chemical Thermodynamics*, p. 81. Trouton's work of 1884 was anticipated also by Pictet (1876) and by Ramsay (1877).

We can now apply the first latent heat equation, and write

$$dT = \frac{T\,dp(v_2 - v_1)}{L} = \frac{353 \times 1013000 \times 0 \cdot 146}{35 \cdot 6 \times 4 \cdot 18 \times 10^7}$$
$$= 0 \cdot 0351° \text{ C. per atmosphere.}$$

QUESTIONS

Chapter XXXI

1. Prove the formula which gives the change in melting point of a substance when the pressure is increased.   (St. A. U.)

2. The heat equivalent of fusion of mercury is 560 cal. for one mole and the melting point is 234·1° K. What is the change of entropy on fusion ?

Assuming that at the melting point the density of solid mercury is 14·19 and of liquid mercury is 13·69 gm. per c c , calculate the change in the melting point for a pressure of 1 atmosphere. Atomic weight of Hg = 200·6.

3. Calculate the specific volume of the vapour of ethyl ether, $C_2H_5OC_2H_5$, at the boiling point from the following approximate data :

Boiling point, 34·6° C. at 1 atmosphere. Latent heat, 86 calories per gram. Density of liquid, 0·71 gm. per c c., dp/dt, 27 mm. of mercury per degree C.

4. Show on a p-v diagram the isothermals of a substance which contracts on melting, indicating the relative temperatures of the isothermals drawn. By consideration of a Carnot cycle, show how the variation of melting point with pressure depends upon the contraction of the substance with melting.   (L.U., B.Sc)

5. Explain what is meant by the term entropy.

Prove that if unit mass of liquid (specific heat c) at temperature T_0 is heated to temperature T and vaporised at the latter temperature, the change of entropy is $c \log (T/T_0) + (L/T)$, where L is the latent heat of vaporisation.

6. Define the term " specific heat of a saturated vapour ". Given that the latent heat of vaporisation of water at $t°$ C. is $(596·73 - 0·601t)$ cal. gm.$^{-1}$, calculate the specific heat of saturated steam at 100° C., and discuss the nature of your result. Prove any relation employed in the calculation. [Specific heat of water at 100° C. = 1·007.]   (L.U., B.Sc.)

7. The boiling point of benzene is 80° C. under a pressure of 760 mm. of mercury, and it is found that a rise of 1° C. in the boiling point takes place for an increase in pressure of 23·5 mm. Show by thermodynamic reasoning that this is a necessary consequence of the expansion which takes place on vaporisation. Calculate this expansion, assuming the latent heat of vaporisation to be 95 calories per gram.

8. Discuss the second law of thermodynamics. Establish thermodynamically an expression by means of which the variation of the boiling point of a liquid with pressure may be calculated when the latent heat of vaporisation and the densities in the liquid and gaseous states are known.   (L.U., B.Sc.)

9. What is meant by the *latent heat of fusion,* and the *latent heat of evaporation* ? How can they be measured ?

To 10 grams of ice initially at – 10° C., heat is supplied at the rate of 1 cal. per sec. until it is completely converted into steam. Draw a diagram of the temperature against time. How will the diagram be changed if the external pressure is increased ?   (E.U., M.A.)

10. Deduce an expression for the change of boiling point of a liquid produced by a change of pressure on its surface.

Calculate the change in pressure in mm. of mercury necessary to change the boiling point of water from 99·5° to 100·5° C., given that the latent heat of steam is 540 cal. per gm. and that the specific volume of saturated steam at 100° C. is 1660 c.c. per gm.   (L.U., B.Sc.)

11. Show from thermodynamic principles that a rise in the boiling point of a liquid with increase in pressure is a necessary consequence of the expansion which takes place on vaporisation.

12. Given that the specific volumes of ice and water at 0° C. are 1·0908 and 1·0001 c.c. per gm. respectively, prove that the freezing point of water will be lowered by increase of pressure, and calculate the change in freezing point for a change in pressure of 10^6 dynes per sq. cm.   (L.U., B.Sc.)

13. Prove that $\partial p / \partial T = L/(v_2 - v_1) T$, where the symbols have their usual significance. Water boils at 100·5° C. and 99·5° C. when the atmospheric pressures are respectively 77·371 and 74·650 cm. of mercury. Calculate the volume of a gram of steam at 100° C., the latent heat being 537 cal./gm.   (L.U., B.Sc.)

14. Discuss the effect of pressure on the melting point of a solid.

Calculate the change in the melting point of naphthalene per atmosphere change of pressure, given : melting point 80° C., latent heat 35·5 calories per gram, density of solid 1·145, density of liquid 0·981.   (E.U., M.A.)

15. Discuss the thermal effect of the application of pressure to a body, finding an expression for the change of temperature when the process is adiabatic.

How has the theory been verified experimentally ?   (E.U., M.A. Hons.)

16. Derive an expression showing how the difference of the specific heats of a liquid and its saturated vapour varies with the absolute temperature.

Apply it to the case where the latent heat of vaporisation is given by

$$L = a + b\theta + c\theta^2.$$ (E.U., Inter. Hons.)

17. Investigate the first latent heat equation (Clapeyron-Clausius).

Assuming that the saturated vapour obeys the gas laws and the specific volume of the liquid may be neglected compared with that of the vapour, show that

$$\frac{1}{p}\frac{dp}{dT} = \frac{\lambda_e}{RT^2},$$

where λ_e is the latent heat of evaporation.

18. The density of iodine at the boiling point (185·3° C.) is 3·71 gm. per c.c. and the latent heat of vaporisation is 40·2 cal./gm. If the boiling point changes by 1° C. for a change in pressure of 17 mm. of mercury, calculate the specific volume of the vapour.

CHAPTER XXXII

THERMODYNAMIC FUNCTIONS AND RELATIONS

General thermodynamic relations. Our object in thermodynamics is to discuss the state of a system and the changes which occur in passing from one state to another. For this purpose we introduce certain variable quantities with a view to specifying a particular state. Such quantities are, for example, p, v, T, S, U. Since we do not require all these quantities at one and the same time to determine that state, there must be certain relations between the variables. These relations we now proceed to consider.

Perfect differentials. First it will be necessary to make a digression, that we may understand clearly what is meant in mathematics in speaking of a **perfect differential.** Let us suppose that we have a certain quantity z depending upon two other quantities x and y, so that z is some function of x and y. Mathematically we express this saying that $z = f(x, y)$. Take two axes at right angles as the axes of the coordinates Thus for any particular point A, with coordinates x, y, the quantity z has some particular and definite value. It might have several values for this particular point, but we shall suppose that z is a single-valued function of x and y. Then z is completely determined by the instantaneous values which the two variables x and y possess at any moment. We then say that dz is a **complete** or **perfect differential.** Provided this is the case, when we go from a point A to a point C on the diagram (Fig. 242), the value of z at C will be independent of the actual path pursued. There are any number of paths from A to C, but the value of z changes in going from A to C by an amount which is independent of the path traversed. It follows that if we take the quantity z through a cycle, such as $ABCDA$, the value of the " cyclic integral " $\oint dz$ will be 0.

Let us choose infinitesimal changes dx and dy in the variables x and y
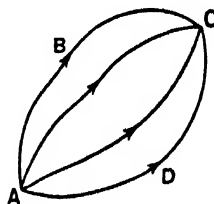
FIG. 242. GEOMETRICAL REPRESENTATION OF A PERFECT DIFFERENTIAL

Draw the elementary rectangle $ABCD$ (Fig. 243), the coordinates of A being x, y, and the sides of the rectangle dx or dy.
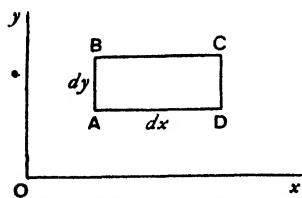
FIG. 243. ELEMENTARY
RECTANGLE $dx \cdot dy$

In the diagram, AB is dy, AD is dx, the coordinates of D will be $x+dx$, y; the coordinates of B will be x, $y+dy$; and the coordinates of C will be $x+dx$, $y+dy$.

Suppose we choose the path ABC from A to C. Then if the value of the quantity is z at A its value at B will be $z+\dfrac{\partial z}{\partial y}\,dy$.

The value of z at C will be

$$\left(z+\frac{\partial z}{\partial y}\,dy\right)+\frac{\partial}{\partial x}\left(z+\frac{\partial z}{\partial y}\,dy\right)\times dx.$$

Secondly, let us use the path ADC from A to C. The value of z at D will be $z+\partial z/\partial x\,dx$. The value of z at C will be

$$\left(z+\frac{\partial z}{\partial x}\,dx\right)+\frac{\partial}{\partial y}\left(z+\frac{\partial z}{\partial x}\,dx\right)\times dy.$$

Now, if dz is a complete differential, this result must be the same as the previous one, that is,

$$z+\frac{\partial z}{\partial x}\,dx+\frac{\partial z}{\partial y}\,dy+\frac{\partial^2 z}{\partial y\,\partial x}\,dx\,dy=z+\frac{\partial z}{\partial y}\,dy+\frac{\partial z}{\partial x}\,dx+\frac{\partial^2 z}{\partial x\,\partial y}\,dy\,dx,$$

and therefore,

$$\frac{\partial^2 z}{\partial y\,\partial x}=\frac{\partial^2 z}{\partial x\,\partial y}.$$

This relation holds good *only* when dz is a perfect differential. This, then, is the mathematical condition that must be satisfied for dz to be a perfect or complete differential. When this condition holds, we may employ the distinctive notation $\mathbf{d}z$ for the *perfect* differential. The meaning of this mathematical expression is that we can carry out the two processes of differentiation in either order without affecting the final result.

Theorem. Let it be given that $\mathbf{d}z = X\,dx + Y\,dy$, where both X and Y, and also z, are functions of x and y.

Then $$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y.$$

Proof. Since z is a function of x and y, we write $z=f(x, y)$.

$$\therefore\ \mathbf{d}z=\left(\frac{\partial f}{\partial x}\right)_y dx+\left(\frac{\partial f}{\partial y}\right)_x dy.$$

So $$X=\left(\frac{\partial f}{\partial x}\right)_y\quad\text{and}\quad Y=\left(\frac{\partial f}{\partial y}\right)_x;$$

$$\therefore\ \left(\frac{\partial X}{\partial y}\right)_x=\frac{\partial^2 f}{\partial y\,\partial x}=\frac{\partial^2 f}{\partial x\,\partial y}=\left(\frac{\partial Y}{\partial x}\right)_y.$$

PERFECT DIFFERENTIALS IN THERMODYNAMICS

Now let us consider some illustrations of such perfect or exact differentials in the realm of thermodynamics.

(1) **Temperature in the gas equation.** We know that for a perfect or ideal gas, the equation of state is

$$pv = RT,$$

and the three variables p, v and T are connected by this mathematical relation, R being a constant. Consequently the temperature T is equal to pv/R, and the value of the temperature is known when p and v are given. If we bring the gas back to the same condition of pressure and volume after any cycle of change, the temperature returns to its initial value. Starting with the equation $T = pv/R$, differentiate with regard to p, and we have $\partial T/\partial p = v/R$.

If we now differentiate with regard to the volume, keeping the pressure constant, we write the result,

$$\frac{\partial}{\partial v}\left(\frac{\partial T}{\partial p}\right) = \frac{1}{R}.$$

Next consider another series of changes. First change the volume keeping the pressure constant, then $\partial T/\partial v = p/R$. If we now change the pressure keeping the volume constant, we have $\dfrac{\partial}{\partial p}\left(\dfrac{\partial T}{\partial v}\right) = \dfrac{1}{R}$, as above, so that in this case we do find the result,

$$\frac{\partial}{\partial v}\left(\frac{\partial T}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial T}{\partial v}\right).$$

Consequently $\mathbf{d}T$ is a perfect differential.

(2) **Intrinsic energy.** We have already seen that the fundamental principles of thermodynamics may be expressed by means of two laws. The first law, the law of conservation, may be written

$$dQ = \mathbf{d}U + dA.$$

In this equation U, the internal energy, is completely determined for any state when we know the values of the coordinates which define that state. Thus, $\mathbf{d}U$ is a perfect differential. On the other hand, the external work done during the transformation depends not only on the initial and final conditions, but also on the nature of the intermediate operations, and so dA is not a perfect differential, and it follows from the equation that dQ is not a perfect differential.

(3) **Entropy.** The second fundamental principle of thermodynamics tells us that $dQ = T\,dS$. The entropy S is a property of the system determined by the coordinates which fix that particular state. In any

reversible cycle $\oint dS = 0$, so we see that dS is a perfect differential. If dS is a perfect differential, it follows that dQ/T may be regarded as a perfect differential. Consequently, although dQ is not a perfect differential, when it is multiplied by $1/T$ we obtain a quantity which *is* a perfect differential, and the factor $1/T$ is spoken of as an integrating factor. In a complete cycle we have

$$\oint \frac{dQ}{T} = 0.$$

Geometrical representation of thermodynamic functions. In the case considered above, where z is a function of the two variables x and y, a very convenient representation of the function is obtained by employing the geometry of three dimensions and representing z as the vertical height above the xy plane, assumed horizontal. This mode of representation has been employed by J. Willard Gibbs in dealing with thermodynamic functions.

Any *three* of the quantities p, v, T, S, U may be taken as rectangular coordinates (xyz) of a point P in space. As the substance passes through all possible conditions of equilibrium, the point P describes a certain surface. This surface exhibits the characteristic properties of the substance and may be called a *characteristic* surface.
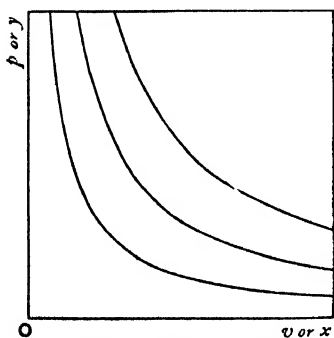
FIG. 244. SECTION OF CHARACTERISTIC SURFACES

As an example, p, v, T may be taken as coordinates. For a perfect gas, we have $pv = RT$, corresponding to $xy = Rz$.

The resulting characteristic surface is a rectangular hyperbolic paraboloid asymptotic to the planes xz and yz (Fig. 244).

The v, S, U surface has been studied by J. Willard Gibbs. This thermodynamic surface is described in Maxwell's *Theory of Heat*, Chapter XII.

MAXWELL'S THERMODYNAMIC RELATIONS

Independent variables.

I. $\left(\dfrac{\partial T}{\partial v}\right)_S = -\left(\dfrac{\partial p}{\partial S}\right)_v$; S, v.

II. $\left(\dfrac{\partial S}{\partial v}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_v$ T, v.

III. $\left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial v}{\partial S}\right)_p$ S, p.

IV. $\left(\dfrac{\partial S}{\partial p}\right)_m = -\left(\dfrac{\partial v}{\partial T}\right)$ T, p.

The four equations stated above are known as **Maxwell's Relations.** They were numbered by him in 1871 in the reverse order and represent certain connections between the *four* variables p, v, S and T according to the choice made of the *two* independent variables. The relations can be deduced either by an analytical or by a geometrical method.

Geometrical method of establishing Maxwell's four thermodynamic relations. This method is illustrated in the four diagrams, Figs. 245, 246, 247 and 248.

(*a*) **Independent variables T and p.** Consider a cycle $ABCD$ bounded by two consecutive isothermals T and $T+1$, and two consecutive adiabatics S and $S+1$ (Fig. 245).
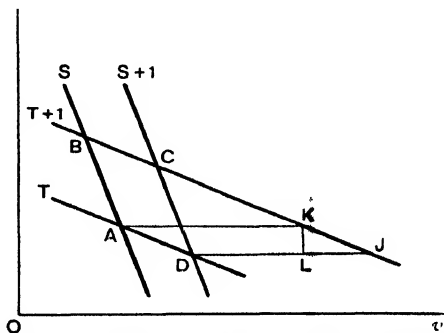
FIG. 245.   FOURTH THERMODYNAMIC RELATION

We shall treat the quadrilateral $ABCD$ as a parallelogram. Draw AK and DJ parallel to the v-axis, and KL parallel to the p-axis.

The area of $ABCD$ is unity, since $((T+1)-T)((S+1)-S)=1$. Now, since they are parallelograms on the same base AD, and between the same parallels,

$$ABCD - AKJD = 1,$$
$$\therefore \ AK \times KL = 1.$$

Now AK represents the increase of volume at constant pressure when the temperature increases by unity,

$$\therefore \ AK = \left(\frac{\partial v}{\partial T}\right)_p .$$

KL represents the decrease in pressure as we pass from A to D along the isothermal. In this change the entropy increases by unity.

$$\therefore \ KL = -\left(\frac{\partial p}{\partial S}\right)_T ;$$
$$\left(\frac{\partial v}{\partial T}\right)_p \times \left(-\frac{\partial p}{\partial S}\right)_T = 1 ;$$
$$\therefore \ \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right). \qquad \text{.IV}$$

(b) **Independent variables S and p.** Next draw AM and BN parallel to the axis of v and AL at right angles (Fig. 246).

As before, $$ABCD = ABMN = 1 ;$$
$$\therefore AM . AL = 1.$$

* AM represents the increase of volume at constant pressure when the entropy is increased by unity,

$$\therefore AM = \left(\frac{\partial v}{\partial S}\right)_p .$$

AL represents the increase in pressure as we pass from A to B along the adiabatic. In this change the temperature increases by unity,

$$\therefore AL = \left(\frac{\partial p}{\partial T}\right)_S ;$$

$$\therefore \left(\frac{\partial v}{\partial S}\right)_p \times \left(\frac{\partial p}{\partial T}\right)_S = 1 ;$$

$$\therefore \left(\frac{\partial v}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S . \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots III$$

(c) **Independent variables T and v.** Now draw AE and DF parallel to the axis of p, and AG parallel to the axis of v (Fig. 247).
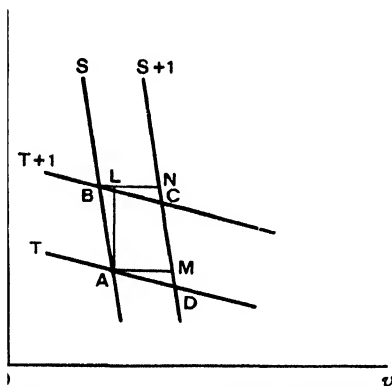
FIG. 246. THIRD THERMODYNAMIC
RELATION
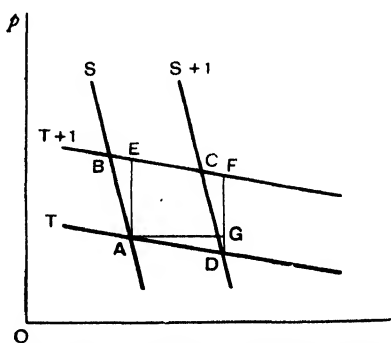
FIG. 247. SECOND THERMODYNAMIC
RELATION

As before, $$ABCD = AEFD = 1 ;$$
$$\therefore AE \times AG = 1.$$

AE represents the increase of pressure at constant volume when the temperature is increased by unity,

$$\therefore AE = \left(\frac{\partial p}{\partial T}\right)_v .$$

AG represents the increase in volume as we pass from A to D along the isothermal. In this change the entropy increases by unity,

$$\therefore\ AG = \left(\frac{\partial v}{\partial S}\right)_T;$$

$$\therefore\ \left(\frac{\partial p}{\partial T}\right)_v \times \left(\frac{\partial v}{\partial S}\right)_T = 1\ ;$$

$$\therefore\ \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T.\dots\dots\dots\dots\dots\dots\dots\dots\text{II}$$

(d) **Independent variables S and v.** Lastly, draw AL, BM parallel to the axis of p and AN parallel to the axis of v (Fig. 248).
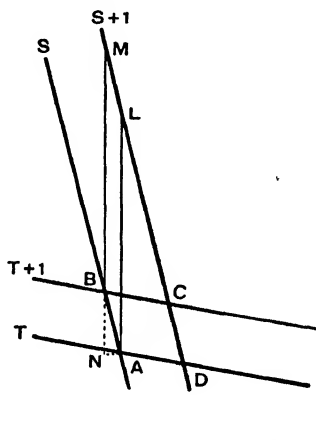
FIG. 248.   FIRST THERMODYNAMIC RELATION

As before,
$$ABCD = ABML = 1\ ;$$
$$\therefore\ AL \times AN = 1.$$

AL represents the increase of pressure at constant volume when the entropy is increased by unity,

$$\therefore\ AL = \left(\frac{\partial p}{\partial S}\right)_v.$$

AN represents the decrease in volume as we pass from A to B along the adiabatic. In this change the temperature increases by unity,

$$\therefore\ AN = -\left(\frac{\partial v}{\partial T}\right)_S;$$

$$\therefore\ \left(\frac{\partial p}{\partial S}\right)_v \times \left(-\frac{\partial v}{\partial T}\right)_S = 1\ ;$$

$$\therefore\ \left(\frac{\partial p}{\partial S}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_S.\dots\dots\dots\dots\dots\dots\dots\dots\text{I}$$

As Maxwell points out, these four relations are not independent of one another, so as to rank as separate truths. They will be proved by a different method in the following pages.

THERMODYNAMIC FUNCTIONS

The condition of a system may be specified by means of certain selected variables, such as p, v, T, or S. Between the variables certain relations exist. The two laws of thermodynamics provide two relations which may be written : $dU = dQ - dA$ and $dQ = T\,dS$. For a complete knowledge of the system some other relation is required ; such a relation, for example, is provided by the equation of state of a fluid. But in general, when such an equation of state is not available, certain functions of the variables may be introduced for the purpose of simplifying the mathematical operations connected with a change in the condition of the system. These functions may be called the **thermodynamic functions**. We shall proceed to discuss the four principal thermodynamic functions, and in each case we shall be able to deduce one of Maxwell's relations by an analytical process.

I. **Intrinsic energy.** We have already introduced such a function in the quantity U, which we have called **internal** or **intrinsic energy**, defined by the equation $dU = dQ - dA$. If we suppose that the change takes place at uniform external pressure, p, we may write $p\,dv$ for the external work dA, and then we have $dU = dQ - p\,dv$. For dQ we substitute $T\,dS$ and so obtain $dU = T\,dS - p\,dv$, the variables employed being S and v. It is assumed in the definition of entropy that the transformation is reversible. In the particular case, where the volume is kept constant, dv is zero, and we have $dU = T\,dS = dQ$.

Returning to the general case, $dU = T\,dS - p\,dv$, and taking partial differentials of the intrinsic energy, we have

$$\left(\frac{\partial U}{\partial S}\right)_v = T, \quad \left(\frac{\partial U}{\partial v}\right)_S = -p.$$

But since dU is a perfect differential, we may apply the mathematical criterion obtained previously (p. 650). We thus find

$$\frac{\partial}{\partial v}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial v}\right);$$

$$\therefore \left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_v . \quad \dots\dots\dots\dots\dots\dots\dots\dots\text{I}$$

This result we have already obtained. It is the first thermodynamic relation.

II. **Free energy for isothermal processes.** There is another thermodynamic function which has been called by Helmholtz, the free energy F.

The **Helmholtz free energy**, F, is defined by the equation

$$F = U - TS.$$

It follows from this definition that the value of F depends only on the state of the substance and dF is a perfect differential.

Hence
$$dF = dU - d(TS)$$
$$= dU - T\,dS - S\,dT.$$

But
$$dU = T\,dS - dA.$$

Hence
$$dF = -S\,dT - dA.$$

Putting $dA = p\,dv$, we have

$$dF = -S\,dT - p\,dv.$$

where T and v are the independent variables. It follows that the partial differentials of F are

$$\left(\frac{\partial F}{\partial T}\right)_v = -S, \quad \text{and} \quad \left(\frac{\partial F}{\partial v}\right)_T = -p.$$

Since dF is a perfect differential,

$$\frac{\partial}{\partial v}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial v}\right).$$

Hence
$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{II}$$

which is the second thermodynamic relation.

III. **Enthalpy, or total heat.** The function H, now known as the enthalpy, is defined, as we have seen previously (p. 564), by the equation

$$H = U + pv.$$

The value of H does not depend on the path by which a state is reached, but only on the state itself.

On differentiation, we find
$$dH = dU + d(pv)$$
$$= (T\,dS - p\,dv) + (p\,dv + v\,dp)$$
$$= T\,dS + v\,dp,$$

where S and p are the independent variables.

The partial differentials of H are

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_S = v.$$

Applying the condition for dH to be a perfect differential,

$$\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right),$$

we obtain
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial v}{\partial S}\right)_p, \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\text{III}$$

which is the third thermodynamic relation.

IV. Gibbs function. Last of all we have a thermodynamic function, now generally known as the **Gibbs function.** This function, G, is defined by the equation

$$G = U - TS + pv.$$

The function G depends only on the actual state of the substance.

On differentiation we find

$$dG = dU - d(TS) + d(pv)$$
$$= (T\,dS - p\,dv) - (T\,dS + S\,dT) + (p\,dv + v\,dp)$$
$$= v\,dp - S\,dT.$$

Here the independent variables are p and T.

The partial differential coefficients of G are

$$\left(\frac{\partial G}{\partial p}\right)_T = v, \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_p = -S.$$

Now dG is a perfect differential, so that applying the criterion

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right),$$

we find

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T, \quad\dots\dots\dots\dots\dots\dots\dots\text{IV}$$

which is the fourth thermodynamic relation.

We notice that these four thermodynamic functions U, F, H, G lead to the four relations of Maxwell.

The number of mathematical relations between the various properties of a system is very great. Bridgman * has developed a method of facilitating the calculation of such expressions.

SUMMARY
Thermodynamic Functions

Intrinsic energy (or Internal Energy).

$$dU = dQ - dA.$$
$$dU = T\,dS - p\,dv. \qquad \text{(variables } S \text{ and } v.)$$

Free energy for isothermal processes (or Helmholtz Free Energy).

$$F = U - TS.$$

Gibbs " force function for constant temperature ", ψ.

$$dF = -S\,dT - p\,dv. \qquad \text{(variables } T \text{ and } v.)$$

Enthalpy (or Total Heat).

Heat Function, $\qquad H = U + pv.$

Gibbs " heat function for constant pressure ", χ.

$$dH = T\,dS + v\,dp. \qquad \text{(variables } S \text{ and } p.)$$

Gibbs function (or Thermal Potential).

$$G = U - TS + pv.$$

Gibbs " force function for constant pressure ", ζ.

$$dG = v\,dp - S\,dT. \qquad \text{(variables } T \text{ and } p.)$$

G bears the same relation to F that H does to U.

The four quantities $U,\ U - TS,\ U - TS + PV,\ U + PV$ "are all cognate and should be regarded as on a parity in the sense that they are all potentials, so that by suitable differentiations of each, any of them can yield the complete state of a substance, entropy or temperature, pressure or volume, thermoelectric current or e.m.f." (International Conference, 1934.)

Notation adopted for the thermodynamic functions. It is unfortunate that the notation adopted for the thermodynamic functions has not been uniform, and in some cases is liable to lead to confusion.   In this book the recommendations of the *International Conference on Physics* (London, 1934) have been followed.   It is necessary to point out that some American writers, following Lewis and Randall (*Thermodynamics*, 1923), use E for U, A for F, and F for G, so that great care is required in interpreting the results of published papers.   Table 48 has been drawn up to show the symbols employed by different investigators.

TABLE 48
Symbols for Thermodynamic Functions

	Entropy	Internal energy	Free energy	Gibbs function	Enthalpy
Adopted - - -	S	U	F	G	H
Callendar - - -	ϕ	E	—	G	H
Clausius - - -	S	U	w	—	—
Ewing - - -	ϕ	E	—	G	I
Gibbs - - -	η	ϵ	ψ	ζ	χ
Lewis and Randall -	S	E	A	F	H
Preston - - -	ϕ	U	$\mathcal{F}$	Φ	—

Some properties of the thermodynamic functions. It is desirable at this stage to recapitulate the more important results reached and to state some further relations involving thermodynamic functions.   This is the more necessary on account of the diversity of definition and notation found in various text-books.

Intrinsic Energy, U

This conception depends on the first law of thermodynamics and is *defined* by the equation $dU = dQ - dA.$

The external work dA can usually be expressed by the typical term $p\,dv.$

Entropy, S

This involves the second law of thermodynamics, and the definition of change of entropy is expressed by

$$dS = dQ/T.$$

Enthalpy, or Total Heat, H

This function, H, is defined by the equation

$$H = U + pv.$$

Willard Gibbs, who represented this function by the Greek letter χ, called it the heat function for constant pressure. It has often been called the " total heat " or " heat content ", but the name **enthalpy,** suggested by K. Onnes, is to be preferred. The function enthalpy is of particular importance in the thermodynamics of engineering.

As the definition shows, the enthalpy is equal to the sum of the internal energy and a certain amount of external work pv. This is " the external work which would be done if the substance could be imagined to start from no volume at all and to expand to its actual volume, under a constant pressure equal to its actual pressure " (Ewing).

Starting from the definition given, we obtain, on differentiating,

$$dH = dU + p\,dv + v\,dp.$$

$$dH = (T\,dS - p\,dv) + p\,dv + v\,dp = T\,dS + v\,dp.$$

Most experimental work in calorimetry is carried out at constant pressure, not at constant volume. In such cases $dp = 0$ and $dH = T\,dS$. This result in some degree justifies the use of the term " total heat " in describing H.

We now consider some further results connected with the functions F and G.

Helmholtz Free Energy, F

The **Helmholtz free energy** F has been called by Maxwell the " available energy ". This function was also employed by Willard Gibbs, who called it the ψ function. It is also called the thermodynamic potential at constant volume. The free energy is defined by means of the equation $F = U - TS$. It follows at once that $U = F + TS$. Here U represents the total internal energy. This equation indicates that this internal energy is made up of two parts, first the free energy F which is available energy in reversible isothermal changes. Planck, in his book on thermodynamics, remarks that F should rather be called the **free energy for isothermal processes.** The second part of the internal energy is represented by TS which, of course, is $U - F$, and this may be called the **latent energy**

or **bound energy** of the system, because it cannot be obtained in useful form.

Employing the terms thus defined, we may say

intrinsic energy = Helmholtz free energy + latent energy.

We notice that, as the entropy S tends to increase, the latent energy also tends to increase, and the free energy tends to diminish.

We have seen that
$$dF = -S\,dT - dA.$$

Consequently when the change considered is a reversible *isothermal* change, i.e. when $dT = 0$, $dF + dA = 0$, this means that in such changes the external work, dA, is done wholly at the cost of the free energy of the system. This shows us why the name " free energy " is appropriate. F is the available energy at constant temperature, and corresponds exactly with the potential energy of a mechanical system. Just as a mechanical system uses up potential energy in doing work, so a system doing work at constant temperature uses up a certain amount of this free or available energy. The change in the free energy is exactly equal to the maximum work done in isothermal changes.

One further result of great importance should be noticed. We have $U = F + TS$. Now $S = -\left(\dfrac{\partial F}{\partial T}\right)_v$. The entropy is the rate at which the free energy changes with temperature, when the volume is kept constant. Substituting this value of S, we get

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_v.$$

This equation was discovered by Thomson in 1855. It is generally known, however, as the Gibbs-Helmholtz equation, having been used independently by Willard Gibbs and by Helmholtz. From the standpoint of the application of thermodynamics to chemical problems, this is one of the most important thermodynamic equations. It does not involve the calculation of entropy, which is often difficult, but it gives an exact quantitative relation between the change in internal energy, U, and the change in free energy, F, occurring during any reversible process.

GIBBS FUNCTION, OR GIBBS FREE ENERGY, G

Last of all we have a thermodynamic function which has been called the thermodynamic potential at constant pressure (Duhem), but is now generally known as the **Gibbs function.** This is defined by means of the equation
$$G = U - TS + pv.$$

This function, G, was called ζ by Willard Gibbs.

We notice that $F = U - TS$, therefore we can write

$$G = F + pv,$$

or, since $$H = U + pv,$$

$$G = H - TS.$$

Writing this equation in the form

$$H = G + TS,$$

we see that if the function G be called the **Gibbs free energy,**

$$\text{enthalpy} = \text{Gibbs free energy} + \text{latent energy.}$$

Both the enthalpy and the Gibbs function are of special importance in experiments carried out at constant pressure.

We have already seen that

$$dG = v\,dp - S\,dT,$$

and consequently $$\left(\frac{\partial G}{\partial p}\right)_T = v, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S.$$

An equation similar in form to the Gibbs-Helmholtz equation in terms of F follows immediately,

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p.$$

APPLICATIONS OF THERMODYNAMIC FUNCTIONS

As an illustration of the application of these functions we consider a perfect gas undergoing an isothermal change.

In general, $dG = v\,dp - S\,dT$. For an isothermal change, $dT = 0$, so that $dG = v\,dp$.

Hence $$G_B - G_A = \int_A^B dG = \int_A^B v\,dp.$$

For a perfect gas, $pv = RT$, so that $v = RT/p$.

$$G_B - G_A = \int_A^B RT\frac{dp}{p} = RT\log_e\frac{p_B}{p_A}.$$

Free energy and chemical affinity. Julius Thomsen in 1853 proposed to take the heat of reaction as a measure of the **affinity** of the reaction, and in 1865 Berthelot put forward a similar principle known as the law of maximum work. These suggestions, which may be regarded as analogous to Kelvin's treatment of the electromotive force of a cell, are not strictly correct, and we now recognise that the correct measure of the affinity is the diminution of free energy.

Conditions for equilibrium. The thermodynamic functions are of practical importance in studying the conditions of equilibrium of a system. We have already seen that in any actual process the entropy of the system concerned tends to increase. In a state of equilibrium every possible infinitesimal process is reversible, and therefore the total entropy

remains constant for such infinitesimal changes. It is a necessary condition for equilibrium that for any process $dS = 0$. This is the most general thermodynamic criterion of equilibrium. It is, indeed, so general in character as to be difficult of application.

In many cases the thermodynamic functions may be employed in practical problems with considerable advantage. For example, just as a mechanical system is in equilibrium when the potential is a minimum, so a system at constant temperature and volume is in stable equilibrium when the function F, the free energy, has a minimum value. For this reason this function is sometimes called the thermodynamic potential at constant volume. Similarly a system at constant temperature and pressure is in stable equilibrium when the function G, the thermodynamic potential at constant pressure, has a minimum value. In this connection we may notice the two equations

$$dF = -p\,dv - S\,dT\,;$$

$$dG = v\,dp - S\,dT.$$

The criterion of equilibrium is that the left-hand side of the appropriate equation has the value zero.

According to the **principle of least energy** when a dynamic system is in stable equilibrium, any change in its state results in conditions opposed to further change in the same direction. Expressed in somewhat different terms Le Chatelier's **law of reaction** (1888) states that when a system in equilibrium is subjected to a constraint, a change takes place within the system tending to annul the effect of the constraint and to restore equilibrium. A still more general statement, that is often of service in physics and chemistry, asserts that every system in equilibrium is **conservative** and tends to remain unchanged.

WORKED EXAMPLES

1. *Prove that corresponding elements of area are equal whether drawn on a p-v diagram or a T-S diagram.*

Let us start with any two independent variables x and y which will determine the state of the substance under examination. Subsequently these symbols may be replaced by any two of the quantities p, v, T and S at pleasure.

Then we may write $dp = \dfrac{dp}{dx}\,dx + \dfrac{dp}{dy}\,dy,$

and three similar expressions for the other quantities, v, T and S.

Let us consider the simple equations which we have already discussed.

$$dQ = dU + p\,dv,$$

and $$dQ = T\,dS.$$

We may combine them in the form

$$dU = T\,dS - p\,dv.$$

As we have seen above, we may write

$$dS = \frac{dS}{dx} dx + \frac{dS}{dy} dy,$$

and

$$dv = \frac{dv}{dx} dx + \frac{dv}{dy} dy,$$

$$\therefore\ dU = \left(T \frac{dS}{dx} - p \frac{dv}{dx} \right) dx + \left(T \frac{dS}{dy} - p \frac{dv}{dy} \right) dy.$$

Consequently it follows that the coefficients of dx and dy in this equation are the differential coefficients of U with respect to x and y respectively, and we may write

$$\frac{dU}{dx} = T \frac{dS}{dx} - p \frac{dv}{dx}, \quad \text{and} \quad \frac{dU}{dy} = T \frac{dS}{dy} - p \frac{dv}{dy}.$$

But since dU is a perfect differential, we know

$$\frac{d}{dy} \left(\frac{dU}{dx} \right) = \frac{d}{dx} \left(\frac{dU}{dy} \right),$$

or

$$\frac{d}{dy} \left(T \frac{dS}{dx} - p \frac{dv}{dx} \right) = \frac{d}{dx} \left(T \frac{dS}{dy} - p \frac{dv}{dy} \right),$$

which leads to the symmetrical relation

$$\frac{dT}{dx} \cdot \frac{dS}{dy} - \frac{dT}{dy} \cdot \frac{dS}{dx} = \frac{dp}{dx} \cdot \frac{dv}{dy} - \frac{dp}{dy} \cdot \frac{dv}{dx}.$$

The geometrical interpretation of this shows that corresponding elements of area are equal whether referred to p and v or to T and S as rectangular coordinates.

The four thermodynamic relations may readily be obtained * from this equation by choosing x and y as any pairs of the four quantities p, v, T, and S.

2. *Prove that for a homogeneous fluid*

$$C_p - C_v = T \left(\frac{dp}{dT} \right)_v \left(\frac{dv}{dT} \right)_p.$$

Hence prove that if the constants a and b in van der Waals's equation may be taken as small, then

$$C_p - C_v = R \left(1 + \frac{2a}{RTv} \right).$$

(L.U., B.Sc. Special.)

Consider a small quantity of heat dQ communicated to the fluid. Let the pressure p remain constant, but let the volume change by dv and the temperature by dT.

We may then write $\quad dQ = \left(\frac{dQ}{dT} \right)_v dT + \left(\frac{dQ}{dv} \right)_T dv.$

But $\left(\frac{dQ}{dT} \right)_v = C_v$, the specific heat at constant volume, and remembering that $dQ = T\,dS$, we have $\left(\frac{dQ}{dv} \right)_T = T \left(\frac{dS}{dv} \right)_T.$

* See Preston, *Theory of Heat*, page 701 (1929).

Applying Maxwell's third thermodynamic relation (No. II in Preston's ːt on p. 652), we find that this is equal to $T\left(\dfrac{dp}{dT}\right)_v$.

$$\therefore\ dQ = C_v dT + T\left(\frac{dp}{dT}\right)_v dv;$$

$$\therefore\ \left(\frac{dQ}{dT}\right)_p = C_v + T\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_p.$$

But $\left(\dfrac{dQ}{dT}\right)_p = C_p$, the specific heat at constant pressure,

$$\therefore\ C_p - C_v = T\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_p.$$

For a **perfect gas**, we have $pv = RT$,

$$\therefore\ \left(\frac{dp}{dT}\right)_v = \frac{R}{v}, \quad \text{and} \quad \left(\frac{dv}{dT}\right)_p = \frac{R}{p};$$

$$\therefore\ C_p - C_v = T\times\frac{R}{v}\times\frac{R}{p} = R.$$

For a gas which obeys **van der Waals's equation**, we have

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{v-b};$$

$$\therefore\ \left(\frac{dp}{dT}\right)_v = \frac{R}{v-b}, \quad \text{and} \quad \left(-\frac{2a}{v^3} + \frac{RT}{(v-b)^2}\right)\left(\frac{dv}{dT}\right)_p = \frac{R}{v-b};$$

$$\therefore\ C_p - C_v = \frac{T\cdot\dfrac{R}{v-b}\cdot\dfrac{R}{v-b}}{\dfrac{RT}{(v-b)^2} - \dfrac{2a}{v^3}} = \frac{R}{1 - \dfrac{2a}{v^3}\cdot\dfrac{(v-b)^2}{RT}}.$$

The last term in the denominator shows the divergence from the case of the perfect gas.

But since b is very small in comparison with v, we may write as an approximation

$$C_p - C_v = \frac{R}{1 - \dfrac{2a}{RTv}}, \quad \text{or, since } a \text{ is also small,} \quad = R\left(1 + \frac{2a}{RTv}\right).$$

QUESTIONS

CHAPTER XXXII

1. If the changes in temperature and volume of a system are dT and dv corresponding to the reception of a small amount of heat dQ, prove that

$$\left(\frac{\partial Q}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v.$$

Hence prove that when a perfect gas expands isothermally heat must be supplied in amount exactly equivalent to the external work done by the gas in the expansion.

2. Establish the four thermodynamic relations.

Derive expressions for the variation of internal energy with volume for

(a) a gas obeying van der Waals's equation $\left(p + \dfrac{a}{v^2}\right)(v - b) = RT$;

(b) general systems in terms of the coefficient of expansion and the bulk modulus.

* Show that for any substance, the difference between the specific heat (c_p) at constant pressure p and at atmospheric pressure $a\,(c_a)$ is given by the relation

$$c_p - c_a = -T \int_a^p \left(\frac{\partial^2 v}{\partial T^2}\right)_p dp.$$

(E.U., M.A. Hons.)

3. If C_p and C_v are the specific heats at constant pressure and constant volume respectively, prove that

$$\frac{1}{C_v} - \frac{1}{C_p} = -\frac{1}{T}\left(\frac{dT}{dv}\right)_S \left(\frac{dT}{dp}\right)_S.$$

4. If E_T and E_S are the isothermal and adiabatic elasticities respectively, and C_p is the specific heat at constant pressure, prove that

$$\frac{1}{E_T} - \frac{1}{E_S} = \frac{T_v}{C_p}\left(\frac{1}{v}\frac{dv}{dT}\right)_p^2.$$

5. Explain the meaning of the terms " intrinsic energy ", U, and " free energy ", F, and show that

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_v.$$

Discuss the importance of this equation in chemical work.

Employing a function Z defined by $Z = F + pv$, and a function H defined by $H = U + pv$, show that

$$Z = H + T\left(\frac{\partial Z}{\partial T}\right)_p.$$

(E.U., M.A. Hons.)

6. Define the two free energy functions F and G, and explain the importance of these functions. Deduce from them the corresponding thermodynamic relations of Maxwell. (St. A. U.)

7. Write an account of the " free energy " of a system, distinguishing between the Helmholtz and the Gibbs expressions for this energy.

Explain the meaning and importance of " free energy ", pointing out the difference between the two functions F and G.

One gram-molecule of a perfect gas is heated from $0°\,C.$ to $100°\,C.$ Find the changes in F and G when (a) the volume is kept constant at 1 litre, (b) the pressure is kept constant at 1 atmosphere.

8. An isothermal change takes place represented on the indicator diagram by a curve joining two points A and B. Show how to obtain a simple representation on the diagram of the change in the function F and in the function G.

9. Show that the first latent heat equation may be derived by assuming the truth of one of Maxwell's thermodynamic relations.

10. From Maxwell's fourth thermodynamic relation deduce a value for the change of temperature due to the adiabatic compression of a liquid.

CHAPTER XXXIII

APPLICATIONS OF THERMODYNAMICS

THERMODYNAMIC reasoning is of great generality, a fact which is at once the source of its power and its difficulty. In the present chapter we deal with some applications to very different phenomena.

    (1) Electrochemistry.

    (2) Surface tension and surface energy.

    (3) The stretching of a wire.

    (4) The thermodynamics of the atmosphere.

(1) THERMODYNAMICS AND ELECTROCHEMISTRY

The recommendations of the International Conference on Physics (1935) as to thermal units are important in dealing with the applications of thermodynamics to electrochemistry. When heat is regarded as energy the unit approved is the **joule**, defined as 10^7 ergs.

The thermal unit is the **gram-calorie**, which is the quantity of heat required to raise the temperature of 1 gram of water from $14\frac{1}{2}°$ C. to $15\frac{1}{2}°$ C.

The connection between these units is given by Joule's equivalent, and the value representing the experimental results is quoted as $4\cdot18_6$ joules per calorie. In this book we have employed the value $4\cdot18_5$, which is that adopted by Birge (1929) in discussing a number of physical constants and the relations between them.

The importance of the **joule** in electrochemistry is due to the fact that the *practical* units of electrical quantities are defined in such a way that energy in joules is equal to the product of volts and coulombs. When there is a difference of potential of 1 volt between two points, 1 joule of work is performed for each coulomb of electricity transferred between the two points. Thus, in general, $W = EQ$, where W is the energy in joules, E the potential difference or electromotive force in volts, and Q the quantity of electricity in coulombs.

$$\text{Joules} = \text{volts} \times \text{coulombs,}$$

Since $Q = It$, or the product of the current and the time, we may also write $W = EIt$, or, using practical units,

$$\text{joules} = \text{volts} \times \text{amperes} \times \text{seconds}.$$

The unit for measuring activity or rate of doing work is the watt (1 joule per second) so that

$$\text{watts} = \text{volts} \times \text{amperes}.$$

By employing the practical units given above, which form a consistent set of units related to the joule as unit of work, it is unnecessary to introduce the C.G.S. electromagnetic units of electrical quantities and much confusion is avoided.

Faraday's laws of electrolysis. When an electric current is passed through a voltameter the mass M of any substance liberated is directly proportional to the quantity Q of electricity traversing the voltameter. This is known as Faraday's first law of electrolysis. From this law it follows that

$$M = zQ, \quad \text{or} \quad M = zIt,$$

where z is a *factor of proportionality*, to which the name **electrochemical equivalent** is given. This factor is found by experiment to be constant for a given substance, that is, the value of z does not depend on the size of the voltameter, or of the electrodes, or on their distance apart.

We shall suppose that M is measured in grams and Q in coulombs, so that the electrochemical equivalent is expressed in grams per coulomb. Thus the electrochemical equivalent of silver is 0·001118 gm. per coulomb.

We now consider a number of voltameters containing different electrolytes joined in series, and suppose the same current is passed through each for the same time, so that the same number of coulombs traverses each voltameter. Observation of the masses of the different substances leads to Faraday's second law, which states that the mass of any substance liberated is proportional to the **chemical equivalent** of that substance. By this term we mean the mass of an ion, or radicle, which will replace, or combine with, one part by mass of hydrogen. In the case of an element, the chemical equivalent is found by dividing the atomic weight by the valency. For example, in a cupric salt such as copper sulphate ($CuSO_4$), copper (atomic weight 63·57) has valency 2 and the chemical equivalent is 31·78$_5$; while for silver, which has valency 1, the chemical equivalent is the same as the atomic weight, 107·88. It is clear from the statement of the two laws just given that the electrochemical equivalent of any substance must be proportional to its chemical equivalent.

If we consider a mass of any substance containing as many grams as there are units in the chemical equivalent we may call this mass the **gram-equivalent** of the substance. According to the laws of electrolysis

a gram-equivalent of *any* substance is liberated by the passage of a fixed amount of electricity through the electrolyte. This quantity of electricity has been called the **faraday** (F_0), and it is believed to be a general constant of nature. The gram-equivalent of silver (Ag) is equal to its atomic weight (107·88) in grams. The amount of silver deposited in electrolysis by one international coulomb is 0·001118 gm., so that we find

$$F_0 = \frac{107\cdot88 \text{ gm.}}{0\cdot001118 \text{ gm./coulomb}}$$
$$= 96494 \text{ international coulombs.}$$

For many calculations it is sufficiently accurate to assume that

$$F_0 = 96500 \text{ coulombs.}$$

It should be noticed that since each gram-equivalent transports one faraday in electrolysis, *two* faradays are transported by one gram-atom of a bivalent substance, three faradays are transported by one gram-atom of a trivalent substance, and so on.

According to modern ideas, each univalent ion carries a charge numerically equal to the electronic charge e. The Avogadro number, N_0, gives the number of atoms in the gram-equivalent of such an ion. Hence one may define the faraday as equal to the product $N_0 e$.

Application of thermodynamics to electric cells. We can in general apply thermodynamic reasoning to any process which is reversible, and in particular such reasoning may be applied to certain electric cells. All cells are not reversible, as for example the simple voltaic cell, consisting of a plate of copper and a plate of zinc in dilute sulphuric acid (H_2SO_4). When the cell is producing electrical energy, zinc goes into solution and hydrogen is evolved at the copper electrode. If a current from an external source is passed through the cell in the opposite direction to that in which the cell normally gives a current, copper is dissolved and hydrogen is produced at the zinc electrode. Reversing the current does not therefore restore the initial state, and consequently the cell is irreversible.

Daniell cell. The Daniell cell, however, is found to be reversible. It consists essentially of a copper jar, which acts as one electrode, containing a saturated solution of copper sulphate ($CuSO_4$) and a porous pot containing a zinc rod surrounded by dilute sulphuric acid (H_2SO_4) and zinc sulphate ($ZnSO_4$) solution, which is placed inside the copper vessel containing the $CuSO_4$ solution. When the cell is producing electrical energy, $ZnSO_4$ is formed and some of the $CuSO_4$ is decomposed, resulting in a deposit of copper on the copper electrode. On passing an external current in the opposite direction (i.e. from Cu to Zn in the electrolyte), the deposited copper re-dissolves and zinc is deposited from the $ZnSO_4$

solution. This restores the initial conditions, and so the process may be taken as reversible.

It should, however, be noticed that this is only true in the limiting case when the irreversible processes actually present are so small as to be negligible.

Such irreversible processes are the production of heat in the cell in accordance with Joule's law, and the diffusion taking place when there are two liquids in the cell. In practice this means that the current passing must be very small, so that the experimental conditions approximate to those obtaining when the cell is on open circuit. However, in the ordinary method of measuring the electromotive force of a cell by means of a potentiometer, this condition is satisfied after adjustment has been made so that no current passes through the galvanometer. We may therefore expect the potentiometer method to give results in fair agreement with the theory.

The electromotive force of a cell can be calculated from the heat of reaction of the processes involved and the temperature coefficient of the electromotive force. When this coefficient is very small or negligible, the calculation is simple, as was first pointed out by Kelvin.

Kelvin's discussion of the E.M.F. of a cell. In 1851 Kelvin calculated the electromotive force of a Daniell cell on the assumption that the electrical energy arises solely from the chemical changes occurring in the cell.

Let H be the total heat of reaction in calories when a quantity of electricity Q is taken from a cell of electromotive force E. Then $JH = EQ$ or $E = JH/Q$, where J is Joule's equivalent $4 \cdot 185$ joules per calorie. [Volts = joules/coulombs.]

If F_0 is the Faraday constant, and n the valency of the metal forming the negative pole, we may write $Q = nF_0$, so that

$$E = JH/nF_0.$$

Substituting $F_0 = 96494$ coulombs we find, for a univalent metal,

$$E = \frac{4 \cdot 185 H}{96494} = \frac{H}{23057} \text{ volts,}$$

and for a bivalent metal

$$E = \frac{H}{46114} \text{ volts.}$$

Voltaic cells generally depend on exothermic reactions in which the chemical change is accompanied by the *evolution* of heat. Such a change is the formation of zinc sulphate, using zinc and dilute sulphuric acid, the heat of formation per gram-molecule being 37730 calories. On the other hand, copper sulphate is an endothermic compound, but in the Daniell cell copper sulphate is decomposed and copper is deposited, the process

of decomposition being accompanied by an evolution of heat amounting to 12400 calories per gram molecule. Thus the *total* heat of reaction is the sum of these two quantities, or 50130 calories. Since both copper and zinc are bivalent metals, it requires a quantity $2F_0$ coulombs of electricity to complete a reaction involving one gram-atom of copper and of zinc. Hence the electromotive force as calculated by Kelvin's method*

$$= \frac{50130}{46114} = 1\cdot09 \text{ volts.}$$

This result is in good agreement with the observed value, which ranges between $1\cdot07$ and $1\cdot14$ volts, depending on the concentration of the solutions.

The agreement found in the case of the Daniell cell depends on the fact that the temperature coefficient of the electromotive force is very small for this cell. In general the calculation is not so simple, and, as we shall now show, the electromotive force depends on two terms, the first being given by the heat of reaction of the processes involved, while the second is proportional to the temperature coefficient of the electromotive force.

Theory of Helmholtz. It was Helmholtz who gave the more general theory of the voltaic cell, pointing out that thermal electromotive forces may be present in the cell in addition to that due to the heat of reaction. His result may be deduced most readily by assuming the truth of the Gibbs-Helmholtz equation in the form *

$$U = F - T\left(\frac{\partial F}{\partial T}\right)$$

The volume changes accompanying the action of such cells are usually small, and we shall neglect them, assuming that the process takes place at constant volume. The change in total internal energy U corresponds to the heat of reaction which we have called H. The free energy change F may be represented by nEF_0, for the quantity of electricity passing may be taken as nF_0, and the work which the cell can perform at constant temperature is the product EQ.

Thus the Gibbs-Helmholtz equation becomes

$$JH = nEF_0 - TnF_0\frac{\partial E}{\partial T},$$

or

$$E = \frac{JH}{nF_0} + T\frac{\partial E}{\partial T},$$

* It may be remarked here that as we are concerned only with *changes* in the values of U and F, many writers indicate such changes by placing the symbol *delta*, $\varDelta$, before the corresponding quantity, and write the equation as

$$\varDelta U = \varDelta F - T\left(\frac{\partial F}{\partial T}\right)_v$$

which is the general equation required. Practical units are convenient, and E is usually measured in volts, F_0 in coulombs.

When H is expressed in calories, we put $J = 4 \cdot 185$ joules per calorie.

For the Daniell cell U and F are very nearly equal, but this only means that $\dfrac{\partial E}{\partial T}$ is very nearly zero for the cell, that is, the electromotive force is practically independent of temperature.

Alternative derivation of the Helmholtz equation. It is instructive to deduce the Helmholtz equation for the electromotive force of a cell in a more direct manner. We assume that the cell is reversible and suppose it taken through a complete cycle consisting of two isothermal and two adiabatic processes.

(1) We imagine the cell placed in a chamber kept at uniform absolute temperature T. In this condition its electromotive force will have some definite value E. When a small quantity of electricity de has passed through the cell, the work done by the cell is $E\,de$. This work is equal to the heat drawn from the source, Q in mechanical units, together with the heat liberated in the cell by the passage of the charge de through it. Since this is heat accompanying the chemical reactions in the cell (*not* the Joulian heat, which is neglected) we may assume that it is proportional to de and call it $q\,de$. Consequently, in energy units, we have

$$E\,de = Q + q\,de.$$

(2) We now transfer the cell to a chamber with walls that are non-conductors of heat. In this chamber let an adiabatic process occur, in which the cell furnishes a further charge at the expense of its own energy while its temperature falls by a small amount from T to $T - dT$.

(3) We next place the cell in a chamber at this lower temperature $T - dT$, and pass a current in the opposite direction to the first until the same amount of electric charge de has passed through the cell. At this temperature the electromotive force will be $E - \dfrac{dE}{dT}\,dT$, and the work done *on* the cell (which is reversible) will be

$$\left(E - \frac{dE}{dT}\,dT\right)de.$$

(4) We transfer the cell once more to the chamber with walls that are heat insulators, and by passing a charge through it raise its temperature adiabatically so that its final temperature is T.

Every stage in this cycle may be regarded as reversible, provided the operations are carried out in a suitable manner.

The work done in the cycle is approximately equal to the difference

between $E\,de$ and $\left(E - \dfrac{dE}{dT}\,dT\right)de$, that is, $de\dfrac{dE}{dT}\,dT$, for, provided dT is infinitesimal, we may regard the amounts of work in the adiabatic changes as equal and opposite.

We now apply the second law of thermodynamics in the form

$$\frac{\text{work done in cycle}}{\text{heat energy from source}} = \frac{dT}{T},$$

giving

$$de\frac{dE}{dT}\,dT \qquad dT$$

or

$$Q = deT\frac{dE}{dT}.$$

Substituting this value for Q in the first equation we find

$$E\,de = deT\frac{dE}{dT} + q\,de,$$

or

$$E = q + T\frac{dE}{dT},$$

which is the equation of Helmholtz in energy units.

The value of q may be expressed in the form JH/nF_0 previously employed.

This equation has been confirmed experimentally for a number of cells.

(2) SURFACE TENSION AND SURFACE ENERGY

Many phenomena indicate that the interface between a liquid and a gas, or between a liquid and a solid, is in a condition differing from that of the bulk of the liquid. There are two ways of regarding such effects, from the standpoint of superficial tension or from that of superficial energy. These physical hypotheses lead in the end to the same mathematical expression. In many cases the former leads more directly to equations expressing the conditions of equilibrium, but the latter has the advantage of showing more clearly the physical principles.

The surface tension of an interface is the tangential force acting along the interface on a line of unit length in the interface, the force acting normally to the line. In C.G.S. units the surface tension is expressed in dynes per centimetre.

From the point of view of energy, the surface tension may be defined as the change in surface energy per unit change in area. This may be expressed in ergs per square centimetre, a quantity having the same physical dimensions as the previous one.

As we shall see, surface tension is the mathematical equivalent of the *free* energy of the surface.

Surface tension and temperature. It is known that the surface tension of a liquid varies with temperature and, for all liquids, *diminishes* as the temperature rises, becoming zero at the critical temperature. Any change in the area of a film involves the performance of work by or against surface tension.

It follows, from the principles of thermodynamics, that such change must be accompanied by thermal changes.

Let us imagine a heat engine which works by the change of surface tension with temperature (Fig. 249). Let σ_1 and σ_2 be the values of the
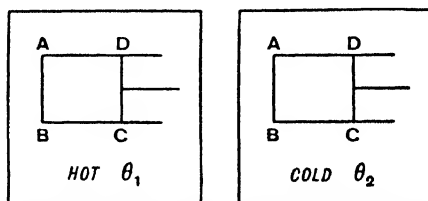
FIG. 249. HEAT ENGINE DEPENDENT ON SURFACE TENSION

surface tension at the temperatures θ_1 and θ_2. Let these two temperatures be so near together that the amount of heat required to raise the temperature of the body from θ_2 to θ_1, is *small compared with the heat involved due to change of area.*

We now suppose the following operations performed. Place the film, which is stretched on a frame $ABCD$, in the hot chamber. Increase the area by A by pulling out the sliding piece CD. Then the work done in stretching the film $= 2\sigma_1 A$ (the factor 2 is introduced because the film has two sides).

Let the heat absorbed in the hot chamber be Q_1.

Now place the film in the cold chamber. Let it contract by the same amount, A.

The work done by the film in contracting $= 2\sigma_2 A$. It is to be noticed that, since $\sigma_2 > \sigma_1$, this amount of work is *greater* than that done in the hot chamber.

Let the heat given out in cold chamber be Q_2.

We may now replace the film in the hot chamber and repeat the cycle.

The two laws of thermodynamics give the following results :

First law $\qquad Q_1 - Q_2 = 2(\sigma_2 - \sigma_1)A.$

Second law $\qquad \dfrac{Q_1}{\theta_1} = \dfrac{Q_2}{\theta_2}.$

Hence
$$\frac{Q_1}{\theta_1} = \frac{Q_1 - Q_2}{\theta_1 - \theta_2} = \frac{2(\sigma_2 - \sigma_1)A}{\theta_1 - \theta_2}.$$

We may put $\frac{\sigma_1 - \sigma_2}{\theta_1 - \theta_2} = \beta$, or in the limit $\frac{d\sigma}{d\theta} = \beta$, where β may be called the temperature coefficient of surface tension.

Then
$$\frac{Q_1}{\theta_1} = -2A\beta,$$

or
$$Q_1 = -2A\beta\theta_1.$$

When β is negative, Q_1 is positive, so that when the film is extended heat must be supplied to keep its temperature constant. This means that if no heat is supplied the film will *cool* when extended. In other words, when the enlargement of the surface takes place **adiabatically,** as in a sudden extension, the liquid is cooled, the *surface* energy being increased at the expense of the *internal* energy. When the enlargement takes place **isothermally,** as in a slow extension, heat flows into the film from surrounding bodies to keep the temperature constant.

Let us suppose the increase in area is 1 sq. cm., then the additional *total* surface energy $E = \sigma + Q$ (for a single surface) where

$$Q = -\beta\theta = -\theta\frac{d\sigma}{d\theta}.$$

Thus
$$E = \sigma - \theta\frac{d\sigma}{d\theta}.$$

The surface tension may be identified with the *free* energy of unit area, but not with the *total* energy. Over a considerable range of temperature (provided the temperature is not near the critical temperature) the relation between σ and θ is linear, and approximately $\frac{d\sigma}{d\theta}$ is constant, or $\frac{d^2\sigma}{d\theta^2} = 0$.

Hence
$$\frac{dE}{d\theta} = -\theta\frac{d^2\sigma}{d\theta^2} = 0 \text{ approximately.}$$

This means that the total surface energy of a liquid remains approximately constant even though the temperature is varied considerably.

More accurate expressions have, however, been obtained showing a slight but regular variation with temperature. A more recent expression giving the relation between surface tension and temperature is

$$\sigma = A(1 - b\theta)^n,$$

where n varies slightly from liquid to liquid, but may be taken as 1·2. The quantity b is very accurately the reciprocal of the critical temperature, or $b = 1/\theta_c$.

[This gives a simple method of finding the critical temperature θ_c by determining n and b.]

By employing a relation discovered by Macleod connecting surface tension with the density of the liquid and that of the vapour it is possible to deduce other important results involving surface tension or the total molecular surface energy.

(3) THE STRETCHING OF A WIRE

Change of temperature produced by stretching. If a wire subjected to a constant tension suddenly suffers a considerable increase of tension its length will increase and it will become stretched. It can be shown by experiment that a change of temperature also occurs : in general for metals the temperature falls, but in the case of india-rubber there is a rise of temperature.

This effect can be calculated theoretically by thermodynamic reasoning, and we shall now give a simplified treatment which may serve to illustrate the " groping " method so often used in scientific research. We suppose the wire is hanging vertically with its upper end fixed and its lower end attached to a pan for holding weights. Let the wire be subjected to a stretching force P and let x denote the vertical displacement of the lower end of the wire from the unstretched position. Let the absolute temperature be T. The state of the wire may be regarded as a function of the two independent variables P and T.

Consider a small additional stretching force dP applied to the wire, and let the displacement change by dx and the temperature change by dT.

Then the heat dQ received by the wire is given by

$$dQ = \gamma\, dT + a\, dP,$$

where γ is the thermal capacity of the wire, and a is a constant which depends on the material of the wire. Its numerical value and sign will be discussed later.
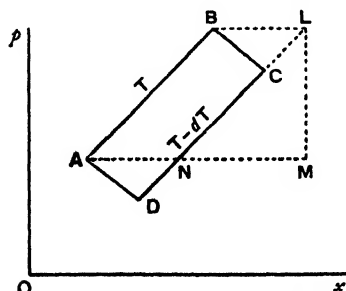
FIG. 250. CARNOT CYCLE FOR THE STRETCHING OF A WIRE

Take the wire round a Carnot's cycle represented on the P-x indicator diagram (Fig. 250). Let AB and CD represent neighbouring isothermals T and $T - dT$, and let AD and BC represent adiabatics.

Let the wire expand isothermally from A to B, taking in a quantity of heat dQ. Then since $dT = 0$, $dQ = a\, dP$.

Now let the wire expand from B to C adiabatically.

Then let it contract isothermally from C to D giving up heat.

Finally, let it contract adiabatically from D to A.

The efficiency of the cycle is $\dfrac{dT}{T}$, and the work done in the cycle is

$$\frac{dT}{T} \times dQ = \frac{dT}{T} \times a\,dP = \frac{a\,dT}{T} \times LM.$$

But we also know that the work done is equal to the area of the cycle

$ABCD = $ area of $ABLN = LM \times BL = LM \times AN = LM \dfrac{dx}{dT}\,dT.$

On equating these two values for the work done, we have

$$LM\frac{dx}{dT}\,dT = \frac{a\,dT}{T} \times LM\ ;$$

$$\therefore\ \frac{dx}{dT} = \frac{a}{T}.$$

Since with few exceptions metals expand as the temperature rises, $\dfrac{dx}{dT}$ is usually positive, and hence a is also generally positive.

If the stretch takes place suddenly, the change may be regarded as at least approximately adiabatic, and we may put $dQ = 0$ in the equation

$$dQ = \gamma\,dT + a\,dP.$$

Hence $\gamma\,dT + a\,dP = 0.$

But we know that for a metal wire γ, a and dP are all positive quantities, and therefore dT must be negative. Hence on stretching such a wire suddenly, its temperature must fall. India-rubber, however, contracts when its temperature is raised. Consequently for it a is negative, and when it is stretched its temperature rises. The indicator diagram (Fig. 250) applies to a case of this kind.

Discussion of the value of the constant a. For an adiabatic change, we have

$$a = -\gamma\frac{dT}{dP}.$$

If we are considering unit cube of the material, we have $\gamma = c\rho$, where c is the specific heat under constant pull (assumed to be nearly the same as the specific heat under no pull) and ρ is the density.

Further, $\dfrac{dT}{dP} = \dfrac{dT}{dx} \times \dfrac{dx}{dP}.$

If β is the change of length under constant load per degree C. rise in

temperature,[*] we have $x_t = x_0(1 + \beta t)$, and on changing to the absolute temperature, this gives

$$dx = x_0 \beta \, dT.$$

$$\therefore \frac{dT}{dx} = \frac{1}{x_0\beta},$$

the length of the wire in its normal condition being x_0.

Further, for an adiabatic change, Young's modulus E_s is defined as

$$E_s = \frac{\text{stress}}{\text{strain}} = \frac{dP}{dx/x_0}, \quad \text{whence} \quad \frac{dx}{dP} = \frac{x_0}{E_s};$$

$$\therefore \frac{dT}{dP} = \frac{1}{x_0\beta} \times \frac{x_0}{E} = \frac{1}{\beta E_s},$$

which leads us to a value for a,

$$a = -\frac{c\rho}{\beta E_s}.$$

The presence of the negative sign in this expression arises from the fact that the argument based on Fig. 250 applies to a substance which contracts as the temperature rises. For a metal such as copper or steel a is positive, as we have seen, and the isothermal for the lower temperature lies above that for the higher temperature. Such a diagram is given by Poynting and Thomson in the passage cited in the footnote. Since work is done by the body in contracting, we must go round the cycle counterclockwise to secure a balance of work done by the body in the cycle.

Numerical values for copper wire. For a copper wire a is positive,

$$\rho = 8.9 \text{ gm. cm.}^{-3}, \quad c = 0.09 \times 4.18 \times 10^7 \text{ ergs gm.}^{-1}{}^\circ\text{C.}^{-1},$$

$$\beta = 1.67 \times 10^{-5}{}^\circ \text{ C.}^{-1}, \quad E = 1.2 \times 10^{12} \text{ dynes cm.}^{-2};$$

$$\therefore a = \frac{0.09 \times 4.18 \times 10^7 \times 8.9}{1.67 \times 10^{-5} \times 1.2 \times 10^{12}} = 1.67 ;$$

It follows that

$$\frac{dx}{dT} = -\frac{1.67}{T}.$$

Thus, if unit length of copper wire at $15°$C., i.e. $T = 288°$ K., is suddenly stretched by 0.01 mm., i.e. $dx = 10^{-2}$ cm., the fall of temperature dT is given by

$$dT = -\frac{288}{1.67} \times 10^{-2} = -1.7° \text{ C.}$$

Consequently, if 100 cm. of the copper wire (a reasonable length for a laboratory experiment) are suddenly stretched by 1 mm., the fall in temperature will be $1.7°$ C.

A method similar to that given above may be employed in investigating the change of temperature due to the adiabatic compression of a liquid. The change is proportional to the coefficient of volume expansion, and

---

[*] More accurately $\beta = \alpha + \phi x$ where α is the ordinary coefficient of linear expansion, ϕ is the coefficient expressing the change of Young's modulus with temperature given by $E = E_0(1 - \phi t)$ (see p. 92), and x is the total stretch already given to the wire. For small stresses, β is approximately equal to α, and the correction may be neglected. See Poynting and Thomson, *Heat*, pp. 302–305.

varies in sign according as this coefficient is positive or negative.   This
result was verified in the experiments of Joule (1859), who observed a rise
in temperature on compressing water at temperatures above 4° C. and
the opposite effect at temperatures below 4° C.

(4) THE THERMODYNAMICS OF THE ATMOSPHERE   ,

In Chapter XXI we gave an account, chiefly from a descriptive point
of view, of certain of the phenomena met with in an investigation of the
properties of the earth's atmosphere.   We are now in a position to make
a further study of some of the more recent meteorological theories which
depend largely upon the thermodynamic conception of entropy.

The atmosphere considered as a heat engine.   On the older views,
which for many years held sway, it was supposed for all practical purposes
that the atmospheric cycle was simply the heating of the air at the hotter
parts of the earth's surface, where it flowed upwards, and the cooling
of the air over the colder polar regions.   Thus the air simply circulated
between the polar regions and the equator, going towards the poles at a
higher level, losing water vapour on the way, and returning at a lower
level as dry air.   This hypothesis gave a satisfactory explanation of how
the air transformed solar heat energy into water power of lakes and rivers
and the energy of the wind, and so long as this was all that it was asked
to explain, it was a good enough working hypothesis.   However, as our
knowledge of the upper atmosphere increased, it was found to be quite
inadequate.

The thermal stratification of the atmosphere.   It was not until about
the year 1921 that a really satisfactory theory of the temperature changes
of the atmosphere was put forward.   In that year Sir Napier Shaw intro-
duced the conception of layers of equal entropy, and showed that the
state of affairs actually in existence in the atmosphere can be represented
by a series of these **isentropic layers** (Fig. 251).   They are nearly, but
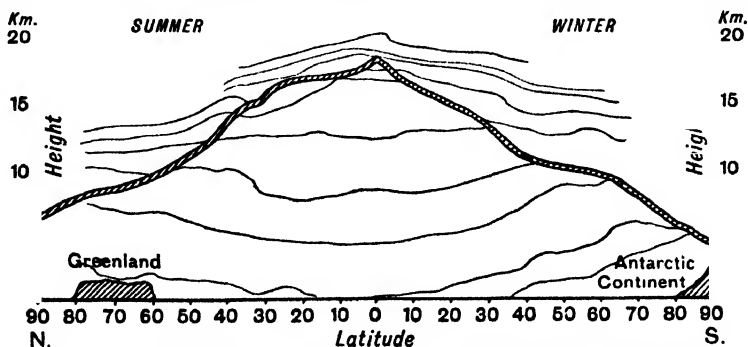
FIG. 251.   ISENTROPIC LAYERS IN A SECTION OF THE UPPER AIR
FROM SOUTH TO NORTH

The shaded band represents the probable position of the tropopause.

not quite, horizontal, and slope upwards slightly from the equator to the poles, particularly in the lower layers. The tropopause is shown in the diagram as a marked surface of discontinuity.*

This conception of Shaw is known as the **thermal stratification of the atmosphere,** because the isentropic layers resemble the strata of geology. Any mass of air retains its original entropy, no matter what its position in the atmosphere, unless heat has been added or extracted. Heat can be added when condensation takes place, the latent heat of vaporisation being involved, or heat can be extracted by loss through radiation. It is found that entropy in the atmosphere bears a close analogy to the density of an incompressible fluid, except that increase in entropy corresponds to diminution of density, and vice versa. The condition of equilibrium is therefore a distribution into horizontal layers, with the air of maximum entropy content uppermost. A mass of air which has been displaced will tend to return to its appropriate entropy layer. Hence the normal atmosphere, in which entropy increases with height, is stable.

It is therefore possible for air to rise only if it receives sufficient heat to raise its entropy to that of the layer to which it is moving. Condensation under normal conditions is found to give so little heat that the corresponding entropy change is only slight. When there is no heat change, air must move along isentropic layers, and we thus get the effect of stratification. This rules out ascending and descending currents, except in the case of very rapid heating and subsequent condensation of the absorbed moisture, such as takes place in the formation of cumulus clouds and similar phenomena, due to what is essentially an adiabatic expansion.

The theory outlined above thus explains the ascent of air to which heat has been supplied. The mechanism for the descent of air is, however, quite different, because there is no process which extracts heat during descent analogous to condensation during ascent. To explain this we must examine further the question of the stratification, because we have noted that there are upward currents, and therefore we must have downward currents under some conditions or other.

If we consider the undisturbed atmosphere at various parts of the world, each has its own stratification due to local conditions of radiation, and other factors varying from place to place. At the equator the stratification is not so close as at the poles. If masses of polar and equatorial air are brought together, the strata will obviously not fit. In fact, they react towards one another like separate immiscible liquids,

* Fig. 251 is largely derived from Shaw, *Manual of Meteorology,* Vol. II, p. 116, Fig. 63 (Second Edition, 1936).

and we have a surface of discontinuity comparable with a geological fault.

The Theory of Margules. Let us consider, as an analogy, two liquids, such as oil and water, which do not mix, and examine how they behave. Then we can apply a similar argument to the two masses of air at different temperatures.

Suppose we have a vessel in the form of a tank containing oil and water as shown in the diagram, separated by a partition (Fig. 252). If we
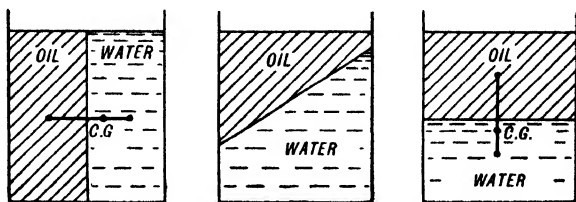
FIG. 252. IMMISCIBILITY OF OIL AND WATER

withdraw the partition and if the density of the water is greater than that of the oil, the water settles down and flows under the oil which rises and flows into a horizontal layer over the water, i.e., the centre of gravity of the system tends to move to as low a level as possible. This change in the position of the centre of gravity releases the energy which sets the liquids in motion. The oil has been lifted, but the important point is that it did not rise through the water, it was pushed up along the surface of discontinuity, which remained clearly marked throughout.

Margules showed that if two masses of air at different temperature are brought together, they react towards one another in the same way as the oil and water in the experiment described, thus releasing the kinetic energy of the atmosphere. The essentially important point in this method of approach is that the two bodies of air which give rise to the energy of the atmosphere never mix, as was supposed on the older theory. Margules calculated that the lowering of the centre of gravity would release sufficient energy to account for the violent atmospheric storms which occur from time to time over the earth's surface.

We can thus explain the descent of the air by a kind of " slipping." We consider the two bodies of air side by side, each with a different stratification of isentropic surfaces. In the warm body of air the corresponding isentropic layers are all lower than in the cold body, and the surface of discontinuity is a sliding surface which no air crosses.

The theory as we have given it above presents the main facts in the simplest form and can only be regarded as a qualitative treatment. In his published works * Shaw also takes into account a great number of

* Shaw, *Manual of Meteorology,* 4 volumes, C.U.P., also *The Air and Its Ways* ; see also Simpson, *Brit. Ass. Report,* 1925, Presidential Address to Section A, where an account of Shaw's work is given.

relevant facts, including the rotation of the earth. On this theory the tropopause may be regarded as a permanent surface of discontinuity.

Entropy-temperature diagram for atmospheric cycle. An important thermodynamic cycle has been obtained by Shaw and Newnham. The diagram * (Fig. 253) is obtained by plotting entropy against temperature for a given specimen of atmospheric air.
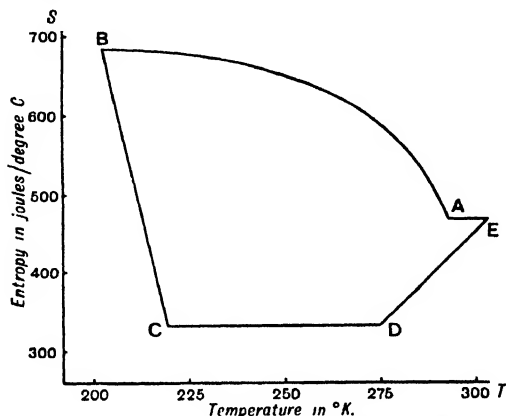
FIG. 253. ENTROPY-TEMPERATURE DIAGRAM FOR ATMOSPHERIC CYCLE

Consider the air starting at A and moving to B, by reason of its natural buoyancy (during this stage it is saturated with water vapour), giving out moisture and absorbing latent heat, thereby obtaining the necessary increase in entropy to enable it to move up to the increased entropy layer which it reaches at B.

BC represents it moving along the tropopause, losing heat by radiation, but nevertheless rising in temperature, since it is compelled to slide along a surface of discontinuity, after the manner of the oil and water. CD represents an isentropic descent (along a stratum).

DE is its journey to the sea, taking in moisture, and rising in temperature, since it is absorbing heat.

EA represents a further isentropic change, restoring it to its original state.

The work done on the environment by the air in the course of the cycle is represented by the area of the closed figure $ABCDEA$, the work being positive or negative according as the cycle is performed in the clockwise or anti-clockwise direction.

We shall conclude this section with some words of Sir Napier Shaw : " Entropy (with water vapour as an accomplice) and air-motion are the

* Fig. 253 is derived from Shaw, *The Air and Its Ways*, p. 155, Fig. 81, but the direction of the temperature ordinate has been reversed in order to conform with the other entropy-temperature diagrams in this book.

joint rulers of the atmosphere ; gravity, pressure, the centrifugal force of rotation whether of the earth or of a local mass . . . are their obedient servants." *

THERMODYNAMICS OF SOLUTIONS

We saw in Chapters IX and X that various physical properties of a liquid were altered when a salt was dissolved in it. For example, it is found experimentally that the vapour pressure of a solution is always less than that of the solvent, that the boiling point is raised and the melting point is lowered. Again, when a semi-permeable membrane is inserted in a vessel, under certain circumstances a difference in pressure, known as osmotic pressure, may be set up between the liquid on either side of the membrane.

These phenomena can all be subjected to thermodynamic treatment, but such treatment belongs rather to the realm of physical chemistry than to pure physics, and the reader is referred to some standard work such as Partington's *Chemical Thermodynamics* for further information on the subject.

WORKED EXAMPLES

1. *The electromotive force of a certain cell containing poles of univalent mercury is* 0·3086 *volt at* 18° *C. and the temperature coefficient is* − 0·00027 *volt per degree. Calculate the total heat of reaction in calories, assuming* $J = 4·185$ *joules per calorie and one faraday* = 96500 *coulombs.*

(St. A.U.)

We have seen above (p. 671) that the Gibbs-Helmholtz equation, which gives the heat of reaction of a cell is given by

$$E = \frac{JH}{nF_0} + T\frac{\partial E}{\partial T}.$$

In this case, $E = 0·3086$ volt, $\partial E/\partial T = -0·00027$ volt/°C., $T = 1 \cdot 5 + 273·2 = 291·7°$ K., $n = 1$, $J = 4·185$ joules/calorie, and $F_0 = 96500$ coulombs.

$$\therefore \ T\frac{\partial E}{\partial T} = 291·7 \times -0·00027 = -0·0788 \text{ volt};$$

$$\therefore \ \frac{JH}{nF_0} = 0·3086 + 0·0788 = 0·3874 \text{ volt};$$

$$\therefore \ H = \frac{0·3874 \times 96500}{4·185} = 8390 \text{ calories}.$$

2. *Determine the radius of the largest drop of water which will evaporate at* 0° *C. when no heat is communicated to it.*

[*Data : Surface tension of water at* 0° *C.* = 75·5 *dynes per cm. Temperature coefficient of surface tension* = − 0·15 *per* °C. *Latent heat of vaporisation of water at* 0° *C.* = 596 *calories per gm. Joule's equivalent* = 4·18 × 10⁷ *ergs per calorie.*]

We found above (p. 675) that the relation between the surface energy E,

* Shaw, *Manual of Meteorology*, Vol. IV, p. viii.

and the surface tension σ, at absolute temperature θ, was given by the equation

$$E = \sigma - \theta \frac{d\sigma}{d\theta}.$$

In this example, $\sigma = 75\cdot5$ dynes/cm., $\theta = 273^\circ$ K., and $\dfrac{d\sigma}{d\theta} = -0\cdot15$.

$$\therefore \ E = 75\cdot5 + 0\cdot15 \times 273 = 116\cdot4 \text{ ergs/cm.}^2.$$

Consider a spherical drop of radius r, and let it shrink by evaporation to a radius $r - \delta r$: thus its radius is decreased by δr.

The area of surface was originally given by $A = 4\pi r^2$; $\therefore$ $\delta A = 8\pi r\, \delta r$.

Thus the decrease in the area of the surface is $8\pi r\, \delta r$;

$$\therefore \text{ the decrease in surface energy} = 8\pi E r\, \delta r \text{ ergs.}$$

Now the decrease in the volume of the sphere due to the shrinkage

$$= \text{area of surface} \times \text{thickness of the layer} = 4\pi r^2\, \delta r.$$

$\therefore$ the decrease in the mass $= 4\pi \rho r^2 \delta r$, where ρ is the density.

Now the heat needed to evaporate this quantity of liquid

$$= \text{mass} \times \text{latent heat} = 4\pi \rho L r^2 \delta r \text{ calories} = 4\pi \rho L J r^2 \delta r \text{ ergs,}$$

where J is Joule's equivalent in ergs per calorie.

Thus, if no heat is supplied from any external source,

$$8\pi E r\, \delta r > 4\pi \rho L J r^2 \delta r; \quad \therefore \ r < \frac{2E}{\rho L J};$$

$\therefore$ the greatest possible value of r is given by

$$r = \frac{2E}{\rho L J} = \frac{2 \times 116\cdot4}{1 \times 596 \times 4\cdot18 \times 10^7} = 9\cdot3 \times 10^{-9} \text{ cm.}$$

QUESTIONS

CHAPTER XXXIII

1. Explain how thermodynamic reasoning may be used in finding an expression for the electromotive force of a primary cell which has a finite temperature coefficient for electromotive force.   (St. A. U.)

2. Apply the laws of thermodynamics to a thermoelectric circuit of two metals a and b, and show that

$$\rho = T\frac{\partial E}{\partial T}, \quad \text{and} \quad \sigma_a - \sigma_b = -T\frac{\partial^2 E}{\partial T^2},$$

where T is the absolute temperature of one junction E, the whole E.M.F. acting in the circuit, and ρ and σ the Peltier and Thomson coefficients respectively.

Show how σ and ρ are represented on the thermoelectric diagram, and describe briefly the method of measurement of the electromotive force in the thermocouple.   (E.U. M.A. Hons.)

3. Prove that if a soap film be stretched heat must be supplied to it if its temperature is to remain constant.

4. Unit mass of elastic material in the form of a wire is suddenly put under tension dT. By applying thermodynamic principles, prove that to keep the temperature from altering when the tension is applied the quantity of heat which must be supplied to the wire is represented by $dQ = al\theta\, dT$, where a is the linear

coefficient of thermal expansion of the material, l is the length, and θ is the absolute temperature of the wire.

Write down the corresponding result for a gas subjected to a sudden increase of pressure.

5. Assuming that the surface tension of water at $0°$ C. is 76 dynes per cm. and at $30°$ C. is 72 dynes per cm., show that, when a water film is extended at room temperature, the mechanical equivalent of the heat required to keep the temperature constant is about half the work done in stretching the film.

6. Investigate the fall in temperature due to adiabatic stretching for a steel wire, as on page 678 for a copper wire, using known values for the physical constants involved.

7. Examine the dimensions of the terms and of the constant a in the equation $dQ = \gamma\, dT + a\, dP$ for the stretching of a wire (page 676) when the equation refers (1) to a wire of given length and area of cross-section, P being in dynes, (2) to unit cube of material, P being in dynes per square centimetre.

8. Prove that when a liquid is suddenly compressed a change of temperature is produced, given by

$$c_p\, dT = T v \alpha\, dp,$$

where dp is the sudden increase of pressure, v is the specific volume, and α is the coefficient of volume expansion at constant pressure.

9. Write a short account of the thermal stratification of the atmosphere, and discuss how the work done in a cycle by unit mass of air may be represented on an entropy-temperature diagram.

THE APPROACH TO THE ABSOLUTE ZERO

VARIOUS experimental methods of obtaining extremely low temperatures have already been described in Chapter XVII, but there are certain theoretical aspects of the subject which deserve further discussion.

According to the kinetic molecular theory, heat consists in the irregular or unordered motion of the smallest particles of matter. This increases with rising temperature, but we can picture a lower limit to the temperature scale, at the point where the thermal motion stops altogether. When we cool down a substance, we increase the internal order of its particles.

We shall now deal with three important methods for cooling, the Joule-Thomson effect, the method of adiabatic expansion, and the paramagnetic method. The last section of this chapter will be devoted to a consideration of the heat theorem of Nernst, a theorem concerned with the various thermodynamic functions near the absolute zero of temperature.

(1) THE JOULE-THOMSON EFFECT

The theory of irreversible expansion. We have seen that Gay-Lussac and Joule carried out experiments in which air compressed in one vessel was allowed to expand into an evacuated vessel. These experiments indicated that on the whole no change of temperature took place. The method is not capable of very accurate results because the heat capacity of the gas is small compared with that of the calorimeter. A more accurate method of experimenting was suggested by Thomson (Lord Kelvin), and between the years 1852 and 1862 a series of experiments was carried out by Kelvin and Joule. These experiments have already been described in Chapter XVII in connection with the liquefaction of gases.

We shall now consider the theory of free expansion, that is to say, the expansion of a fluid when no external work is done during the change of pressure. For simplicity, we may imagine the fluid contained in a cylinder divided into two parts A and B by a partition CD (Fig. 254). Each compartment is provided with a piston, and we assume that the pressure can be measured by determining the force applied to the piston rod. The fluid is forced from the side A to the side B through one or

more small holes or narrow tubes in CD in such a way that the velocity of the fluid is very small shortly after passing through the plug.   The walls of the vessel and the partition are assumed to be constructed of
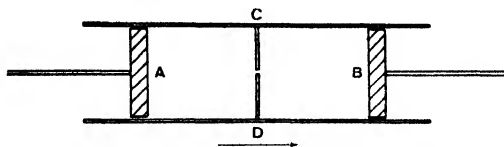
FIG. 254.   THE JOULE-THOMSON EFFECT

non-conducting material.   When the opening is very small the gas passing through under pressure will acquire a considerable amount of kinetic energy.   This arises from the fact that near the orifice there will be an eddy or "rapid" formed by the escaping jet.   But in consequence of the viscosity of the surrounding gas this kinetic energy is quickly lost and transformed into heat.

The work done by the pressure driving the fluid through the plug is spent entirely in overcoming the resistance of the fluid, no heat being supplied to or withdrawn from the fluid.

We have defined (p. 657) a certain function, $H = U + pv$, which is termed the total heat or enthalpy of the fluid.   If we consider unit mass of fluid we may write $h = u + pv$.   It can be shown that this function, the total heat, is unaltered by the passage through the plug.   We may distinguish between the states of the fluid before and after passing through the plug by using subscript letters A and B, i.e. h_A is the total heat per unit mass on one side of the partition, h_B the total heat per unit mass on the other side.   We may imagine the piston A subject to constant pressure p_A, forcing the fluid towards the plug, and the escaping fluid pushing back the second piston which is exposed to constant pressure p_B.   Suppose the first piston moves through a distance corresponding to volume v_A, where v is the specific volume (the volume of unit mass of the fluid), and suppose the second piston moves through a distance corresponding to v_B.   Then if Q is the heat absorbed by unit mass of gas in passing through the plug, the fundamental heat equation,

$$Q = (U_2 - U_1) + A,$$

becomes for unit mass $Q = (u_B - u_A) + p_B v_B - p_A v_A.$

The terms on the right-hand side may be rearranged, giving

$$Q = (u_B + p_B v_B) - (u_A + p_A v_A) = h_B - h_A.$$

But we assume that no heat is supplied from without during the operation, i.e. $Q = 0$, and therefore $u_B + p_B v_B = u_A + p_A v_A,$

or $$h_B = h_A.$$

Thus the total heat or enthalpy is unchanged by the transit through the orifice. Such a process is called by engineers a **throttling process.**

Let us in the first instance assume that the temperature is found to be the same on the two sides of the plug, the temperature on the side B being measured at a sufficient distance from the turbulent region. If Boyle's law holds exactly for the gas under consideration, since $T_B = T_A$ by hypothesis,

$$p_B v_B = p_A v_A; \quad \therefore \ u_B = u_A.$$

This means that the internal energy of the gas is the same on both sides of the porous plug, and consequently is the same at the same temperature whatever the specific volume. If this were found to be the case the assumption made by Mayer in his calculation of the mechanical equivalent of heat would be justified. Actually, however, it is found that the temperature is not exactly the same on the two sides of the porous plug. Some of the results found by Joule and Kelvin are shown in the following table, in which $T_A - T_B = \Delta T$.

<div align="center">

TABLE 49

JOULE-THOMSON EFFECT

</div>

	Expansion between freezing and boiling point (Regnault)	Cooling effect, ΔT per atmosphere
Air - - -	0·36706	$+ 0·208°$
Carbon dioxide -	0·37100	$+ 1·005°$
Hydrogen - -	0·36613	$- 0·039°$

Thus we observe that for air and carbon dioxide the temperature on the side B is lower than the temperature on the side A, but for hydrogen the reverse is true, the temperature of the gas being raised by passage through the plug. In their experiments Joule and Kelvin found ΔT proportional to Δp even for differences of five or six atmospheres. They also found that ΔT varied inversely as the square of the absolute temperature for air and carbon dioxide. If hydrogen is cooled below $-80°$ C. before passing through the orifice it is found to behave in the same way as the commoner gases and ΔT becomes positive. This is called the **inversion temperature.**

Theory of the Joule-Thomson effect. Our object is to obtain a theoretical relation between ΔT and Δp. For the sake of simplicity we assume the pressures on the two sides of the plug to be very slightly different and the difference of all quantities on the two sides of the plug to be represented by using the symbol Δ. In this experiment the

intrinsic energy does not in general remain constant, but the enthalpy h, which is equal to $u + pv$, does remain constant. Consequently $\Delta h = 0$, or $\Delta u + \Delta(pv) = 0$;

$$\therefore \ \Delta u + p\,\Delta v + v\,\Delta p = 0.$$

But since we know that

$$T\,dS = Q = du + p\,dv,$$

we may write

$$T\,\Delta S + v\,\Delta p = 0.$$

Further, the difference in entropy, ΔS, may be expressed in terms of the difference in temperature and the difference in pressure on the two sides of the plug, that is to say, since ΔS is a perfect differential,

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_p \Delta T + \left(\frac{\partial S}{\partial p}\right)_T \Delta p.$$

Substituting these values in the previous equation we get

$$T\left(\frac{\partial S}{\partial T}\right)_p \Delta T + \left(T\left(\frac{\partial S}{\partial p}\right)_T + v\right)\Delta p = 0$$

This equation may be interpreted in a fairly simple way if we notice that $T\left(\frac{\partial S}{\partial T}\right)_p$ is simply C_p, the specific heat at constant pressure. By making use of the thermodynamic relation $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$, (proved above on p. 653), our equation becomes

$$C_p \Delta T + \left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\}\Delta p = 0,$$

or

$$\Delta T = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p} \times \Delta p.$$

This gives us a simple relation between the difference in temperature, ΔT, on the two sides of the plug and the difference in pressure, Δp. The factor $\dfrac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p}$, which occurs on the right-hand side of the equation, is not difficult to determine by direct experiment.

Application to a perfect gas. Let us consider first a particular case, namely that of a perfect gas obeying the ideal gas law $pv = RT$, and maintained under constant pressure. Then, under constant pressure we have $p\left(\frac{\partial v}{\partial T}\right)_p = R$;

$$\therefore \ T\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{p} = v.$$

Thus, under these conditions the numerator of the fraction vanishes, and ΔT is 0.

Application to a non-perfect gas. The form of the expression given above shows at once how it is that the observed value of ΔT may be either positive or negative, for the result depends upon the relative magnitude of the two terms, $T\left(\dfrac{\partial v}{\partial T}\right)_p$, and v.

For any gas ΔT may be found if we know the deviation of the gas from the laws of Boyle and Gay-Lussac. We might, for example, assume that the gas obeys the law of van der Waals, and on that assumption proceed to calculate the value of the numerator of this fraction.

One of the most important applications of the results of such experiments is the determination of the absolute temperature of the melting point of ice.* This temperature is obtained by integrating the equation containing C_p. The values found by Joule and Kelvin, using various gases, are given in Table 50.

TABLE 50

THE ICE-POINT

	Absolute temperature of melting ice
Air - - - -	273·14
Carbon dioxide -	273·9
Hydrogen - -	273

The most accurate results were obtained from the experiments on air. Joule and Kelvin also showed how it was possible to reduce the readings of an air thermometer to the thermodynamic scale ; in other words, the absolute thermodynamic temperature corresponding to any temperature on the air thermometer could be calculated from the experimental results.†

(2) THE METHOD OF ADIABATIC EXPANSION

The adiabatic expansion method of refrigeration. When a quantity of gas under pressure is allowed to expand adiabatically, its temperature is reduced (p. 348). This fact has been made the basis of various methods for liquefying gases. Cailletet (1877) allowed oxygen under pressure

* For a good account of the treatment of this problem by a method of successive approximation see A. W. Porter's monograph, *Thermodynamics*.

† More convenient methods for the calculation of the ice-point and the corrections to the gas thermometer scale have been given by Callendar (*Phil. Mag.*, vol. 5, p. 48, 1903) and by Hoxton (*Phys. Rev.*, vol. 13, p. 438, 1919). These methods are described by Hoare in *A Textbook of Thermodynamics* (1931).

to expand in a glass capillary tube, and observed a mist formed of liquid drops indicating a fall of temperature and the momentary formation of liquid oxygen. Starting at high temperatures the cooling effect obtained is small, but by starting at low temperatures the efficiency of the method is greatly increased.

Let us suppose that the partition CD in Fig. 254 is provided with an aperture of moderate dimensions fitted with a sliding shutter, and that the gas in A is at a high pressure while the gas in B is at a low pressure. When the shutter is removed, the gas in A expands and cooling arises *within the compartment*, apart altogether from the Joule-Thomson effect at the opening in CD. In some forms of liquefier *both* effects are made use of to produce refrigeration.

Claude (1902) used an expansion engine instead of a nozzle. In the liquefier designed by Kapitza for hydrogen and helium a small expansion engine was incorporated in the apparatus. Simon constructed a simple form of helium liquefier, making use of the fact that at very low temperatures the heat capacity of the metal container is extremely small.

(3) THE PARAMAGNETIC METHOD FOR THE PRODUCTION OF VERY LOW TEMPERATURES

A remarkable method * for the production of extremely low temperatures was suggested by Debye and Giauque in 1926. The method has been used with success by de Haas and Wiersma in Leyden and by Kürti and Simon in Oxford.

The theory of the method depends upon a consideration of entropy. The entropy of a substance is a measure of its state of disorder. This way of regarding entropy will be discussed more fully in Chapters XXXIX and XLIII.

If a set of molecules were at rest in an accurate space-lattice, they would be in a state of complete order, and their entropy would be zero. Any change in position or motion would cause the entropy to increase. Let us consider the case of paramagnetic salts ; these contain atoms which behave like small magnets. If their axes are all aligned parallel to one another, their positional state of order will be greater than when they are oriented at random. Let us apply an external magnetic field to such a substance ; then the axes of the magnetic atoms will set themselves parallel to the lines of force, and consequently the entropy due to their positional disorder will decrease. Hence, if the substance is thermally insulated, the entropy due to their thermal motion must in-

* This method is described by Lindemann (*Nature*, 4th May, 1935, pp. 693-5) and by Simon (*Nature*, 11th May, 1935, pp. 777-8). The above account is largely taken from these two papers.

crease ; that is to say, heat will be developed.   Let this heat be carried
away, for example, by placing the substance in contact with liquid
helium, and again let the substance be insulated thermally.   It is clear
that the substance can now be cooled by the removal of the magnetic
field, because in this case the axes of the atomic magnets will tend, under
the influence of thermal agitation, to resume their natural disordered
condition.   The positional entropy will thus increase at the expense of
the entropy of agitation, and consequently the temperature will be
lowered.

Using this method, experiments have been carried out in the region
between 0·03° and 1° K. without difficulty.   Simon, working with iron
ammonium alum and a field of 14,000 gauss, reached 0·04° K., while
at Leyden, where a very strong magnet was available, de Haas was able
to obtain a temperature as low as 0·015° K. with potassium chromium
alum.   Other substances can be examined at these very low temperatures,
if they are mixed with the paramagnetic salt in the form of a small pellet.
By such means abnormalities in the specific heat or the electrical con-
ductivity of these substances at very low temperatures can be detected.

(4) NERNST'S HEAT THEOREM

This theorem was first published by Nernst in 1906, and its importance
is so great that it is now frequently called **the third law of thermodynamics.**
Nernst has published an account of the theorem in a book, translated into
English under the title *The New Heat Theorem.*

Nernst's statement in terms of U and A.   In stating his theorem Nernst
employs two thermodynamic functions U and A that are closely related
to functions we have already considered but are defined in a slightly
different way.

The first law of thermodynamics may be called the Law of Conservation
of Energy.   We have seen already that according to this principle there
is a certain function, U, of the variables which characterise the system,
and this function may be called the intrinsic energy or the internal
energy.   In his book Nernst employs the same symbol to denote the
negative value of the content of energy.   In any change of the system
from some initial state where the energy content is U_1, to a final state
where the energy content is U_2, the change represented by $U_2 - U_1$ is
independent of the route followed.

The second law of thermodynamics may be called the Law of the
Transmutability of Energy.   There are various ways of stating this
principle.   One way is to consider a certain function A, which for
isothermal variations of a system has the same properties as U.   The
symbol A is used by many writers to denote the external work transformed

when any physical or chemical process is carried out reversibly at constant temperature. When the system changes, the quantity $A_2 - A_1$ may be employed to express the maximum external work which can be obtained in the change considered. In isothermal reversible changes the maximum work done will be equal to the diminution of free energy.

The problem of finding the relation between the function A and the function U has long attracted attention. The equation due to Gibbs and Helmholtz may be written

$$A - U = T\left(\frac{\partial A}{\partial T}\right)_v,$$

corresponding to the equation for free energy (p. 661)

$$F - U = T\left(\frac{\partial F}{\partial T}\right)_v.$$

This equation does give a relation between A and U, but it involves the differential coefficient $\frac{\partial A}{\partial T}$. Since this is a differential equation, its solution cannot be regarded as unique. The equation is, however, of fundamental importance in the domain of chemical energetics and the consideration of chemical affinity, and it may be regarded as a summary of the older thermodynamics.

In 1869 Berthelot propounded a law of thermochemistry which may be stated as follows : " Every chemical transformation which takes place without the intervention of external energy tends towards the production of that substance or system of substances which will give the greatest development of heat." Expressed in mathematical symbols this principle of maximum work is equivalent to writing $A = U$, or $A - U = 0$. It has been known for a considerable time that although this result holds approximately in many cases, it is not generally true. If we compare the last equation with the Gibbs-Helmholtz equation we see that the term $T\left(\frac{\partial A}{\partial T}\right)$ must be introduced and may be regarded as a correction to the principle of Berthelot. In some cases this term is very small, but in others it is appreciable. For example, in all systems in which only gravitational, electric or magnetic forces are operative, $\frac{\partial A}{\partial T}$ is zero, and both A and U are independent of temperature. Nernst draws attention to another special case, namely that in which U is zero. Then $A = T\left(\frac{\partial A}{\partial T}\right)_v$. This case is realised in the expansion of ideal gases and the mixture of dilute solutions.

In 1906 Nernst pointed out that, provided $\dfrac{\partial A}{\partial T}$ remains finite at low temperatures, the expression $T\left(\dfrac{\partial A}{\partial T}\right)$ must vanish when $T = 0$, and the Gibbs-Helmholtz equation shows that A and U are necessarily equal at the absolute zero. Nernst assumed that the limiting value of $\dfrac{\partial A}{\partial T}$ and of $\dfrac{\partial U}{\partial T}$ is zero for $T = 0$. The mathematical relation

$$\lim_{T \to 0}\left(\frac{\partial A}{\partial T}\right) = \lim_{T = 0}\left(\frac{\partial U}{\partial T}\right) = 0$$

may be called the **Heat Theorem of Nernst.**

Applications and illustrations. The theorem of Nernst enables us to find the required relation between A and U. According to this theorem A and U must coincide at very low temperatures, and it follows that A is definitely fixed if U is known as a function of the temperature down to the absolute zero. In other words, the new theorem makes it possible to calculate the free energy from purely thermal quantities. In the neighbourhood of the absolute zero U and A remain constant and are identical in value. This may be illustrated by a graphical method. Plot temperatures on the absolute scale horizontally, and energies along the vertical axis (Fig. 255).

Let us assume that the graph for U is some known curve. It may be of the shape shown in diagram (*a*) or of the shape shown in diagram (*b*).
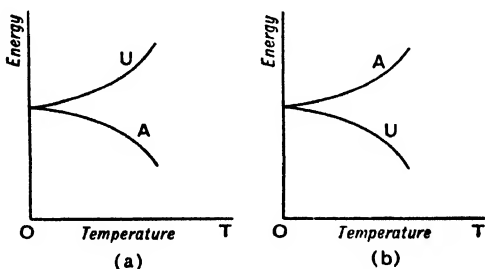
FIG. 255. THEOREM OF NERNST

According to Nernst, *in a condensed system*, the limiting value of $\dfrac{dU}{dT}$ as T approaches the absolute zero is zero, and the limiting value of $\dfrac{\partial A}{\partial T}$ as T approaches the absolute zero is also zero. The theorem implies that if we draw a curve for A the two curves coincide at the absolute zero and they have a common tangent which is horizontal. It follows that if we know the curve for U we can deduce the curve for A either by a graphical method or by calculation.

Returning to the Gibbs-Helmholtz equation, we may write it in the alternative form

$$\frac{\partial}{\partial T}\left(\frac{A}{T}\right) = -\frac{U}{T^2},$$

as may be seen by differentiating the left-hand side of the latter equation. We can now integrate this equation with regard to T, and find

$$\frac{A}{T} = \text{constant} - \int^T \frac{U\, dT}{T^2}.$$

The heat theorem of Nernst implies that this constant of integration is chosen so that the lower limit of the integral is zero.

Therefore,
$$A = -T \int_0^T \frac{U\, dT}{T^2}.$$

If, then, we know U as a function of the temperature we can calculate the value of A. This is frequently done by expanding U as a series in terms of T and thus carrying out the integration. The heat theorem of Nernst gives us information as to the coefficients which appear in the expansion.

Alternative statements of Nernst's heat theorem. There are alternative methods of stating the heat theorem of Nernst. According to Planck a more general form of the theorem is : " The entropy of every actual substance in the pure state is zero at the absolute zero of temperature." In the older thermodynamics entropy was measured from some arbitrary zero. We were not able to fix the absolute value either of the energy or of the entropy of a system of bodies.

In the case of entropy the required information is furnished by Nernst's theorem. The theorem may be stated in the form : " In an isothermal process involving pure solids and liquids the change in entropy approaches zero as the temperature approaches zero." This means that since dS is equal to $\frac{\delta Q}{T}$, δQ must approach the value zero when T approaches the absolute zero of temperature.

The free energy, F, is given by the equation $F = U - TS$, and S is $-\frac{\partial F}{\partial T}$. If, then, the limiting value of $\frac{\partial F}{\partial T}$ when T is zero is equal to zero, it follows that S must approach the value zero when T is zero. This means that the entropy can be represented by a definite integral and not merely by an indefinite integral. We may write

$$S = \int_0^T \frac{C_p\, dT}{T}.$$

This may be regarded as a mathematical statement of the theorem of Nernst.

This form of the theorem leads to an interesting conclusion with regard to the coefficient of expansion. The coefficient of expansion of a chemically homogeneous solid or liquid must be equal to zero in the limit when the temperature approaches the absolute zero.*

The application of Nernst's principle to the enthalpy, H, is of particular interest. It may be assumed that for " condensed " phases (solids and liquids)

$$\lim_{T\to 0} \left(\frac{\partial H}{\partial T}\right)_p = \lim_{T\to 0} C_p = 0.$$

This implies that the integral $\int_0^T C_p \, dT$ can be calculated down to the absolute zero (at least with considerable accuracy) by employing a process of extrapolation from such low temperatures as can be realised experimentally.

Yet another way of stating the new heat theorem is given by Nernst. " It is impossible to devise an arrangement by which a body may be completely deprived of its heat, i.e. cooled to the absolute zero." This law is called by Nernst the " Principle of the Unattainability of the Absolute Zero ". According to this principle, then, we can never hope to reach the absolute zero of temperature, because the nearer we do approach it, the greater becomes the difficulty of further progress.

Lewis and Randall † have discussed the heat theorem of Nernst and conclude that although there is considerable experimental evidence for the theorem in many cases, it has been too hastily generalised. They give the following enunciation : " The entropy of each element in some crystalline state can be taken to be zero at the absolute zero of temperature. Every substance then has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero and does so become zero in the case of perfect crystalline substances, including compounds."

Fowler regards Nernst's theorem as a theorem in statistical mechanics. He states that the theorem can be deduced from statistical mechanics with the aid of a certain extra hypothesis, namely :

The weights of the lowest quantum states of all condensed systems (or, more probably, all pure crystals) are the same.

Assuming this plausible hypothesis, it follows that the entropy changes of reactions in condensed systems (or at least pure crystals) must tend to zero as T tends to o, which is one way of stating Nernst's theorem.

According to Fowler, the existence of an absolute entropy is *not* a consequence of the theorem.

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* For a proof of this theorem see F. E. Hoare, *A Textbook of Thermodynamics*, § 94, p. 164 (1931).

† *Thermodynamics and the Free Energy of Chemical Substances*, p. 448.

QUESTIONS

Chapter XXXIV

1. Give an account of the investigations of Kelvin and Joule relating to the change of temperature which occurs in the throttle expansion of a gas.

Describe briefly one practical application of the effect in question. (L.U., B.Sc.)

2. Write a short account of the experiments of Joule and Thomson on the passage of a gas through a porous plug, and show that the " total heat " or enthalpy remains unchanged in such a process.

3. Give the theory of the Joule-Thomson effect, and point out that the sign of the temperature change depends upon the magnitude of the two terms,

$$T\left(\frac{\partial v}{\partial T}\right)_p \quad \text{and} \quad v.$$

Explain what is meant by *the temperature of inversion.*

4. Give the theory of the porous plug experiment and show that the change in temperature produced is given by the expression

$$\Delta T = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{c} \Delta p.$$

Show how this result may be applied to the problem of correcting the readings of a gas thermometer to the thermodynamic scale.

The temperature of the melting point of ice, recorded by an air thermometer, is $272 \cdot 44°$. What is this temperature on the thermodynamic scale?

The Joule-Thomson cooling for air is $+ \cdot 208°$ per atmosphere.

$[c_p = 0 \cdot 2389$ calories/gm.

$v =$ specific volume at N.T.P $= 773 \cdot 4$ c.c.]   (E U , M.A. Hons.)

5. Write a short account of the liquefaction of gases, giving the essential principles of the Pictet cascade process, the Claude process, and the Linde process.   (St. A. U.)

6. Give an account of the paramagnetic method of obtaining very low temperatures.

7. " The entropy of a substance is a measure of its state of disorder." Discuss this statement, and explain what is meant by saying that the entropy of a perfect crystalline substance becomes zero at the absolute zero of temperature.

8. Nernst's Heat Theorem has sometimes been spoken of as the *Third Law of Thermodynamics.* Discuss the justification for this statement.

Enunciate the theorem in the form which most commends itself to you.

CHAPTER XXXV

MATHEMATICAL THEORY OF CONDUCTION

In Chapters XVIII and XIX we considered the subject of thermal conductivity from an experimental standpoint. We shall now discuss some of the elementary problems which can be solved theoretically by mathematical analysis.

LINEAR FLOW OF HEAT THROUGH A LONG BAR

1. Before a steady state is reached. (*a*) **Excluding radiation.** Let us consider a long bar, composed of uniform material such as a metal, heated
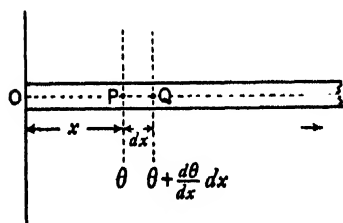
FIG. 256. LINEAR FLOW OF HEAT
THROUGH A LONG BAR

steadily at one end (see Fig. 256), and surrounded by a guard ring so that no heat escapes by radiation. We may conceive the process taking place before a steady state is reached as a temperature wave travelling in a positive direction. The temperature θ at any point P is a function both of the distance from the origin, $OP = x$, and the time t.

Consider two neighbouring cross-sections of the bar at points P and Q on the axis. After a time t, the temperature at P is θ, and the temperature at Q is $\theta + \dfrac{d\theta}{dx} dx$.

For convenience, we shall assume the mathematical convention that θ and x are increasing together.

If A is the area of cross-section of the bar, and K is the thermal conductivity of the material of which it is composed, then

$$\text{rate at which heat is flowing in at } P = -KA \frac{d\theta}{dx},$$

and, rate at which heat is flowing out at $Q = -KA \frac{d}{dx}\left(\theta + \frac{d\theta}{dx} dx\right);$

$$\therefore \text{ the difference} = KA \frac{d^2\theta}{dx^2} dx.$$

This is the rate of increase of heat in the layer, or the gain of heat by the layer in one second.

Now, before the steady state is reached, this heat is employed in raising the temperature of the layer.

Let ρ be the density and c the specific heat of the material of the bar.

Then the mass of the layer which is heated is $A\rho\,dx$, and the heat required to raise the temperature of this mass by $d\theta$ is $A\rho\,dx\,.\,c\,.\,d\theta$.

Therefore, the heat required per second is $A\rho c\,\dfrac{d\theta}{dt}\,dx$.

We can now equate the two expressions we have obtained for this value, and write

$$KA\,\frac{d^2\theta}{dx^2}\,dx = A\rho c\,\frac{d\theta}{dt}\,dx\,;$$

$$\therefore\ \frac{K}{\rho c}\,\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt}\,,$$

or $\qquad\qquad \dfrac{d\theta}{dt} = k\,\dfrac{d^2\theta}{dx^2}\,,\quad$ where $\quad k = \dfrac{K}{\rho c}\,.$

This constant, k, is usually termed the **diffusivity of temperature**, and is of considerable importance. It has already been discussed from the physical standpoint in Chapter XVIII.

The differential equation is known as **Fourier's equation**.

(b) **Including radiation.** We will now treat the same problem assuming that heat escapes from the side of the bar by radiation. In such a case we shall assume that the rate of loss of heat from unit area of surface is given by $E\theta$, where θ is the temperature excess of the surface above that of the surrounding medium,* and E is a constant whose value depends on the nature of the surface. E is usually spoken of as the **surface emissivity**. If p is the perimeter of the section of the bar at P, then the heat lost by radiation in one second from the surface of the element between P and Q will be given by $Ep\theta\,dx$. Therefore the heat required per second to raise the temperature of the mass by $d\theta$ now becomes

$$A\rho c\,\frac{d\theta}{dt}\,dx + Ep\theta\,dx,$$

and the equation obtained above becomes modified into the form

$$KA\,\frac{d^2\theta}{dx^2}\,dx = A\rho c\,\frac{d\theta}{dt}\,dx + Ep\theta\,dx,$$

or $\qquad\qquad \dfrac{d\theta}{dt} = k\,\dfrac{d^2\theta}{dx^2} - \mu\theta,$

where $\qquad\qquad \mu = \dfrac{Ep}{A\rho c}\,.$

* It should be noticed that θ has previously been used to denote the *actual* temperature of the bar. Since, however, the temperature in the preceding discussion only appears as a difference $d\theta$, this does not affect the problem.

2. Steady state. When the rod has been heated for a sufficient length of time, the temperature at every point will become stationary. The steady state has now been reached, and $\dfrac{d\theta}{dt} = 0$.

We may thus write $\qquad k\dfrac{d^2\theta}{dx^2} = \mu\theta,$

or $\qquad \dfrac{d^2\theta}{dx^2} = m^2\theta,$ where $\quad m^2 = \dfrac{\mu}{k} = \dfrac{Ep}{AK}.$

It is now necessary to solve this equation. Again, there are two cases :

(*a*) **Excluding radiation.** Since radiation is to be neglected $\mu = 0$, and consequently

$$\dfrac{d^2\theta}{dx^2} = 0.$$

Integrating this, we have $\qquad \dfrac{d\theta}{dx} = A,$

and, integrating once again, $\qquad \theta = Ax + B,$

showing a linear relationship between x and θ.

A and B are the usual constants of integration, which may be determined from a knowledge of the boundary conditions. For example, if the two ends of a bar of length l, $x = 0$ and $x = l$ are maintained at fixed temperatures $\theta = \theta_0$ and $\theta = \theta_1$, the temperature θ at any point x on the bar can be found by means of the equation

$$\theta = \theta_0 + (\theta_1 - \theta_0)\dfrac{x}{l}.$$

If we regard the end $x = 0$ as the source, $\theta_0 > \theta_1$, and the equation may be written

$$\theta = \theta_0 - \dfrac{\theta_0 - \theta_1}{l}x.$$

The factor $\dfrac{\theta_0 - \theta_1}{l}$ represents the temperature gradient.

(*b*) **Including radiation.** In the more general case, when we cannot neglect the radiation losses, we have

$$\dfrac{d^2\theta}{dx^2} = m^2\theta.$$

To solve this equation, we try a solution of the form

$$\theta = e^{nx}.$$

Then $\qquad \dfrac{d\theta}{dx} = ne^{nx},$

and $\qquad \dfrac{d^2\theta}{dx^2} = n^2 e^{nx}.$

Therefore $n^2 = m^2$, and $n = \pm m$, whence the complete solution is

$$\theta = Ae^{mx} + Be^{-mx},$$

where A and B are constants which have to be evaluated with a knowledge of the boundary conditions of any particular case.

Application to Ingenhausz's experiment. The practical details of this experiment have already been described on p. 391 ; we are now in a position to discuss the mathematical theory underlying it. Bars $A, B, C, \ldots$ of different substances were prepared of the same dimensions and electroplated and polished so as to produce the same surface emissivity E. They were then coated with wax, and their ends immersed in a bath of hot oil at a temperature θ_0. The wax melted for a certain distance along each bar, l_A, l_B, l_C, $\ldots$, until, when the steady state had been reached, the temperature at the end of this distance corresponded with that of the melting point of the wax, θ_1. If the bars are of sufficient length, their cold extremities will be at atmospheric temperature, i.e. $\theta = 0$. Both θ_0 and θ_1 are to be reckoned as excess temperatures above this. We now have three boundary conditions for all the bars :

$$\text{(1) At } x = \infty, \quad \theta = 0 ;$$
$$\text{(2) At } x = 0, \quad \theta = \theta_0 ;$$
and
$$\text{(3) At } x = l, \quad \theta = \theta_1.$$

We now apply these conditions to our equation

$$\theta = Ae^{mx} + Be^{-mx}.$$

From (1), we have $0 = Ae^{m \cdot \infty} + Be^{-m \cdot \infty}$,

and consequently $Ae^{\infty} = 0$, and therefore $A = 0$.

From (2), we have $\theta_0 = Be^{-m \cdot 0}$,   or $B = \theta_0$.

From (3), we have $\theta_1 = \theta_0 e^{-ml}$;

$$\therefore \; ml = \log_e\left(\frac{\theta_0}{\theta_1}\right).$$

Now θ_0 and θ_1 are the same for all the bars, and therefore we may write

$$m_A l_A = m_B l_B = m_C l_C = \ldots \text{ constant.}$$

But, from our definition of m, we have

$$m^2 = \frac{\mu}{k} = \frac{Ep}{A\rho c} \div \frac{K}{\rho c} = \frac{Ep}{KA}.$$

Now the surface emissivity E, the perimeter p and the area of cross-section A have been made identical for all the bars, and therefore we must have

$$\frac{l_A{}^2}{K_A} = \frac{l_B{}^2}{K_B} = \frac{l_C{}^2}{K_C} = \ldots \text{ constant.}$$

This shows that the conductivities of the different substances are directly proportional to the squares of the lengths along which the wax

has melted. Consequently if the absolute value of the thermal con-
ductivity of any one bar is known, the remaining conductivities can
readily be calculated.

Experiments of Despretz and of Wiedemann and Franz. Two early
series of experiments, no longer of any great practical value, are never
theless of considerable theoretical interest in connection with the equation
we have just derived. We shall now make a short digression in order to
describe briefly the experimental arrangements.

So long ago as 1827 experiments were carried out by Despretz on the
relative conductivities of metal bars. The bars were made of the same
size and shape, and, in order to secure at least approximately the same
surface emissivity, were coated with lamp-black, or had white paper
pasted on, or else were electroplated. The bars were heated at one end
by means of a steady lamp (see Fig. 257), and the temperatures at various
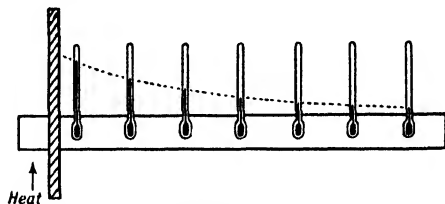
FIG. 257. APPARATUS OF DESPRETZ

equidistant points on the bar were measured by means of thermometers
inserted into small holes sunk into the bar at points on its axis. Good
thermal contact between the thermometer bulbs and the bar was ensured
by placing a little mercury, or at high temperatures a fusible alloy, into
these holes. By such an apparatus the temperature curve along the
entire length of the bar can be obtained.

Despretz's results were not capable of a high degree of accuracy, and
considerable experimental improvements were made by Wiedemann
and Franz in 1854. Their apparatus is illustrated in Fig. 258. The
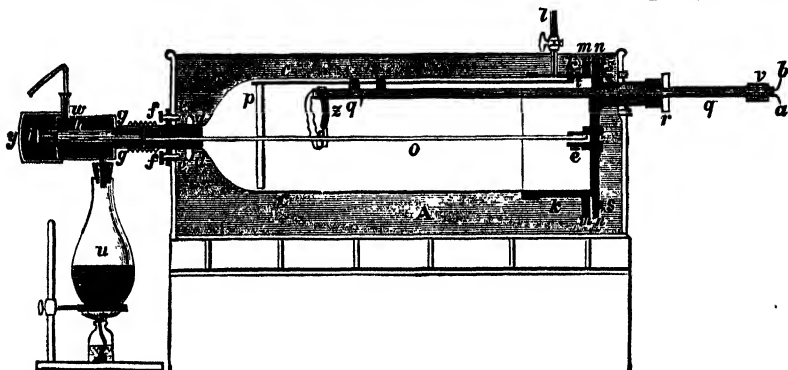
FIG. 258. APPARATUS OF WIEDEMANN AND FRANZ

bars used (o) were about half a metre in length and 6 mm. in diameter. In order to secure uniform surface emissivity they were electroplated. The bar was fixed horizontally in a glass vessel surrounded by a water bath (A), which could be kept at a constant known temperature. The glass vessel could be exhausted so that the experiments could be made either in air or in a vacuum. One end of the bar was heated in a current of steam, and its temperature was thus maintained constant approximately at 100° C. The temperature at any point along the bar was measured by means of the sliding thermocouple z. When a steady flow of heat had been established, the temperatures at three points at equal distances apart were measured.

The theory of these two experiments is similar, and the method of calculating the relative conductivities of bars of different metals from the experimental data will now be described.

Application of the Fourier equation to the experiments of Despretz. In this case we observe the temperatures θ_1, θ_2, and θ_3 at three points on a bar, the distances between two consecutive points being equal. Let the points be situated at distances $x - a$, x, and $x + a$ from the hot end.

We have already seen that the complete solution of the Fourier equation is

$$\theta = Ae^{mx} + Be^{-mx},$$

where A and B are constants of integration. But we also know that the temperature decreases along the bar as we go further away from the hot end, and that, as in the case of Ingenhausz's experiments, $\theta = o$ at $x = \infty$. Therefore, in this case also, the first term vanishes giving

$$\theta = Be^{-mx}.$$

Using our given conditions, we may write

$$\theta_1 = Be^{-m(x-a)},$$
$$\theta_2 = Be^{-mx},$$
$$\theta_3 = Be^{-m(x+a)}.$$

Further, we may write

$$\theta_1 = Be^{-mx}(e^{-m \times -a}) = Be^{-mx} \times e^{ma},$$

and

$$\theta_3 = Be^{-mx}(e^{-m \times a}) = Be^{-mx} \times e^{-ma}.$$

$$\therefore\ \theta_1 + \theta_3 = Be^{-mx}(e^{ma} + e^{-ma}).$$

$$\therefore\ \frac{\theta_1 + \theta_3}{\theta_2} = e^{ma} + e^{-ma} = 2n \quad \text{(say)}.$$

Multiplying this equation throughout by e^{ma}, we have

$$e^{2ma} - 2ne^{ma} + 1 = 0,$$

a quadratic equation in e^{ma}, which on solving yields

$$e^{ma} = n \pm \sqrt{n^2 - 1},$$

or

$$ma = \log_e(n \pm \sqrt{n^2 - 1}).$$

The negative sign before the square root must be rejected. We can see this because, under the conditions of the experiment, $\dfrac{\theta_1 + \theta_3}{2\theta_2} > 1$, and consequently $n > 1$. If we take the negative sign, $n - \sqrt{n^2 - 1}$ becomes less than unity, while e^{ma} is necessarily greater than unity.

Consequently, we must take the positive sign, and write

$$ma = \log_e(n + \sqrt{n^2 - 1}),$$

or

$$\sqrt{\frac{Ep}{KA}}\, a = \log_e(n + \sqrt{n^2 - 1}).$$

Therefore if we consider two bars of different metals of the same perimeter p, cross-section A, and coated so that the surface emissivity E is the same, we can compare their thermal conductivities by means of the equation

$$\sqrt{\frac{K_1}{K_2}} = \frac{\log(n_2 + \sqrt{n_2{}^2 - 1})}{\log(n_1 + \sqrt{n_1{}^2 - 1})} \quad \text{where} \quad n = \frac{\theta_1 + \theta_3}{2\theta_2}.$$

Application to the experiments of Wiedemann and Franz. In the case of Wiedemann and Franz's experiment, the bar can no longer be regarded as infinite in length, and the first term, Ae^{mx}, cannot be neglected. The mathematical analysis thus becomes slightly more complicated, but it is still possible to arrive at the equation

$$\frac{\theta_1 + \theta_3}{\theta_2} = 2n = e^{ma} + e^{-ma},$$

whence the final result follows in exactly the same manner as in the simpler case.

PERIODIC FLOW OF HEAT

Up to this point, we have confined our discussion to the steady flow of heat along a bar which is either jacketed so that no heat escapes by radiation, or else is exposed so that the radiation loss must be taken into consideration. We shall now discuss the situation where the supply of heat at the source is no longer uniform, but is periodic, the end of the bar being alternately heated and cooled. Again there will be two cases, excluding and including the radiation loss. If we exclude radiation and consider the bar to possess a guard ring or jacket, the problem becomes identical with that of the propagation of a periodic temperature wave in one specified direction in a semi-infinite solid. A practical example of this arises in the daily and yearly temperature changes within the surface of the earth.

We may think of the end of such a jacketed bar as being subjected to periodic variations of temperature given by the formula $\theta = \theta_0 \cos \omega t$. Here θ is the temperature measured from its mean value and θ_0 is the amplitude of the variation; ω is the pulsatance $= 2\pi n = 2\pi/\tau$, where n

is the frequency, and τ is the period; and t is the time. The assumption we have made that $\theta = \theta_0 \cos \omega t$ when $x = 0$ implies that in our problem the **mean** value of θ is zero, since for every positive value of $\cos \theta$ there is a corresponding negative value.

We can observe in a general way that the fluctuations of the temperature, at points along the bar may be represented by the type of diagram shown in Fig. 259. This diagram, however, is drawn for a more general case than that we are at present considering and might be used for an unjacketed bar having the mean temperature at the end $x = 0$ higher than the temperature of the far end. The dotted line (which represents the mean temperature) would in the present problem coincide with the axis of x. At any given point the temperature variation at any
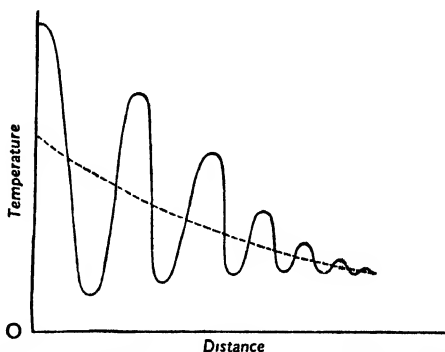
FIG. 259.   PERIODIC FLOW OF HEAT ALONG A BAR, SHOWING DECAYING
AMPLITUDES

time t may be represented by $\theta = a \cos(\omega t - \epsilon)$, where a is the amplitude of the variation, and ϵ/ω is the time lag. This time lag arises from the finite speed of propagation of the temperature wave along the bar, which is due to the heat capacity of the bar. We note further that the amplitude diminishes as the distance along the bar increases, until at a sufficient distance along the bar it may be ignored. At this point the temperature of the bar remains constantly equal to the temperature of the surrounding medium.

We shall now give a mathematical analysis of the above qualitative discussion.

Periodic flow of heat through a long jacketed bar, or in one direction in a semi-infinite solid. Let the direction of flow be along the x-axis, then, as before, the Fourier equation is

$$\frac{d\theta}{dt} = k \frac{d^2\theta}{dx^2},$$

where k is the diffusivity.

Further, we have the conditions that at $x = 0$, $\theta = \theta_0 \cos \omega t$, and since we know that the temperature does not increase as we get further into the solid, we must have at $x = \infty$, $\theta \neq \infty$.

To solve the differential equation, we try a solution $\theta = Ae^{\alpha x + \iota \beta t}$, where $\iota = \sqrt{-1}$, and A, α, and β are constants.

Then, on substituting this value, we have

$$\iota \beta = k \alpha^2, \quad \text{or} \quad \alpha = \pm \sqrt{\frac{\iota \beta}{k}}.$$

Now $\qquad (1 + \iota)^2 = 2\iota$, therefore $\sqrt{\iota} = \dfrac{1}{\sqrt{2}}(1 + \iota).$

Consequently $\qquad \alpha = \pm \sqrt{\dfrac{\beta}{2k}}(1 + \iota),$

and we have $\qquad \theta = Ae^{\pm \sqrt{\frac{\beta}{2k}}(1+\iota)x + \iota \beta t}.$

Since $\theta \neq \infty$ when $x = \infty$, we must reject the positive sign in front of the square root, and take only the negative sign. On separating the real and imaginary parts, this gives

$$\theta = Ae^{-\sqrt{\frac{\beta}{2k}}x + \iota\left(\beta t - \sqrt{\frac{\beta}{2k}}x\right)},$$

which may be written in the form

$$\theta = Ae^{-\sqrt{\frac{\beta}{2k}}x}\left\{\cos\left(\beta t - \sqrt{\frac{\beta}{2k}}x\right) + \iota \sin\left(\beta t - \sqrt{\frac{\beta}{2k}}x\right)\right\}.$$

Now the imaginary term is of no interest to us here and may be rejected. We are thus left with the expression

$$\theta = Ae^{-\sqrt{\frac{\beta}{2k}}x}\cos\left(\beta t - \sqrt{\frac{\beta}{2k}}x\right).$$

At $x = 0$, this becomes $\theta = A \cos \beta t$. But we also know that at $x = 0$, $\theta = \theta_0 \cos \omega t$, and we must thus identify the constant β with the applied pulsatance ω.

Therefore $\theta_0 \cos \omega t = A \cos \omega t$, and consequently, $A = \theta_0$;

therefore $\qquad \theta = \theta_0 e^{-\sqrt{\frac{\omega}{2k}}x}\cos\left(\omega t - \sqrt{\frac{\omega}{2k}}x\right).$

In order to make this equation more general, we can insert an arbitrary constant ϵ in the cosine term, and write

$$\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2k}}x}\cos\left(\omega t - \sqrt{\frac{\omega}{2k}}x - \epsilon\right).$$

This equation represents a wave travelling with velocity $\sqrt{2\omega k}$ (see p. 711), and is illustrated in the diagram, Fig. 259, that has been discussed on p. 705.

Periodic flow of heat in a long bar with radiation from its sides. If the bar is no longer jacketed, and we take into consideration the radiation losses, the Fourier equation is

$$\frac{d\theta}{dt} = k\frac{d^2\theta}{dx^2} - \mu\theta,$$

and, as before, the initial conditions are, at $x = 0$, $\theta = \theta_0 \cos \omega t$; and at $x = \infty$, $\theta \neq \infty$.

To solve this equation we may apply the substitution $\theta = e^{-\mu t}\psi$, and this reduces the problem to the one without radiation that we have already considered.

Applying the substitution, and performing the necessary differentiations, we have

$$-\mu e^{-\mu t}\psi + e^{-\mu t}\frac{d\psi}{dt} = ke^{-\mu t}\frac{d^2\psi}{dx^2} - \mu e^{-\mu t}\psi,$$

whence

$$\frac{d\psi}{dt} = k\frac{d^2\psi}{dx^2},$$

and this equation may be solved in exactly the same way as the previous one.

Ångström's experiments. In 1861 the method of periodic flow of heat was applied by the Swedish physicist Ångström to the measurement of thermal conductivities. He used a long bar AB (Fig. 260), and applied
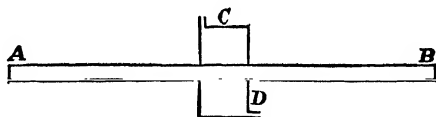
FIG. 260. ÅNGSTRÖM'S APPARATUS

alternate heating and cooling to the centre of the bar by enclosing it in a vessel CD. The bar was heated for twelve minutes by a current of steam, then it was cooled for the same time by a current of cold water, and the process was repeated indefinitely. The periodic time τ was thus 24 minutes, or 1,440 sec., and the frequency $n = 1/\tau = 6 \cdot 9 \times 10^{-4}$ sec.$^{-1}$. After a sufficient time had elapsed, the temperature at any point on the bar became steadily periodic, and the mean temperature became constant. The bar was perforated at intervals of 5 cm. by holes into which thermometers were inserted, and the temperatures at these points were observed.

The elementary theory that we have discussed above treats of a simple harmonic variation of temperature at the hot end of the bar. In

Ångström's experiment, however, the variation is only periodic and not sinusoidal, but it is always possible to expand such a periodic function by means of a Fourier series, which gives an infinite series of sine and cosine terms containing integral multiples of the original frequency n.

The solution of such an equation * becomes

$$\theta = \overset{p=\infty}{\underset{p=0}{\Sigma}} A_p e^{-\alpha_p x} \cos(p\omega t + \beta_p x - \epsilon_p),$$

where $p = 0, 1, 2, 3, \ldots$, and A_p, α_p, β_p, and ϵ_p are constants which can be determined under the actual conditions of the experiment.

King † has employed a modification of Ångström's method for measuring the thermal conductivities of thin wires of copper and tin. One end of the wire is heated electrically by a current whose magnitude varies sinusoidally. Thermocouples replace Ångström's thermometers. The conductivity is calculated from observations on the velocities of two temperature waves of different periods, but for further details both of theory and experiment the original paper should be consulted.

Propagation of temperature waves in the earth's crust. The equation

$\dfrac{d\theta}{dt} = k\dfrac{d^2\theta}{dx^2}$, and its periodic solution $\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2k}}\,x} \cos\left(\omega t - \sqrt{\frac{\omega}{2k}}\,x - \epsilon\right)$,

is of considerable practical importance in measurements on the thermal conductivity of the earth's crust. There are two pronounced periodic temperature variations occurring in nature, and from observations on these it is possible to calculate the conductivity. As the earth rotates on its axis, the surface at any point undergoes periodic heating by day and cooling by night. This is called the **diurnal variation,** and a temperature wave with a period of 24 hours is propagated downwards into the earth. As the earth rotates round the sun, any given point receives a larger amount of heat in the summer than in the winter. Consequently there is an **annual variation,** and a second temperature wave with a period of 12 months is propagated downwards.

Forbes (p. 413) made a series of experiments in Edinburgh, in which he embedded a number of thermometers at different depths in the earth, and was able to investigate the progress of the temperature wave. Kelvin, in 1860, discussed the reduction of these observations and the continued Calton Hill series. From his results he calculated a value of 0·0087 for the diffusivity of garden sand, measured in C.G.S. units.

The temperature wave decreases rapidly in amplitude as we go beneath the surface, and there is also a considerable time lag. For

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* For a fuller treatment of this equation, see Carslaw, *The Conduction of Heat,* p. 42.

† King, *Phys. Rev.*, Vol. VI, p. 437 (1915).

example, the maximum temperature occurs at the surface at 2 p.m. and reaches a depth of 10 cm. at about 5.15 p.m., and 30 cm. at 11.45 p.m. Some of these facts are illustrated in Fig. 261.
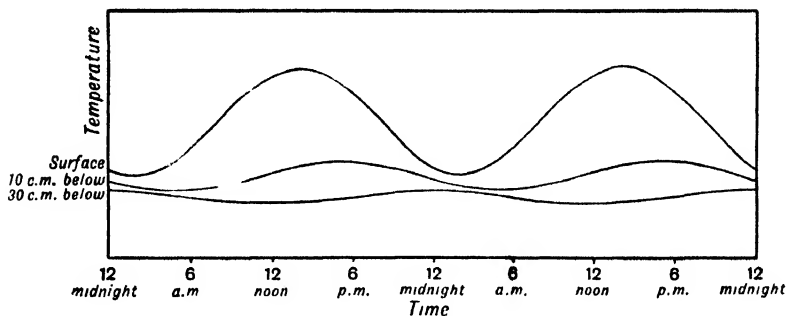
FIG. 261. DIURNAL VARIATION OF THE TEMPERATURE OF THE EARTH'S CRUST

Kelvin also made a calculation of the age of the earth by means of this equation, and obtained the time taken for it to cool from a molten fluid to its present temperature. His result of a hundred million years is far short of the estimate usually given by geologists. A possible explanation of this discrepancy is the fact that the presence of radioactive compounds was then unknown. These all, notably the radium salts isolated by Pierre and Marie Curie, continuously generate heat by spontaneous disintegration, and retard the cooling of the earth. Therefore Kelvin's estimate should be increased very greatly in order to obtain the true age.

THREE-DIMENSIONAL FLOW OF HEAT

We have so far confined our attention to the flow of heat in one direction only. It is beyond the scope of this work to deal with the mathematical proof of the general equations of conduction in three dimensions, and we shall content ourselves with stating the Fourier equation in its general terms.

For a flow of heat in the x-direction only, we have shown that

$$\frac{d\theta}{dt} = k \frac{d^2\theta}{dx^2} .$$

In the general case, this becomes

$$\frac{d\theta}{dt} = k\left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2}\right),$$

which is more generally written in the form

$$\frac{d\theta}{dt} = k \nabla^2\theta.$$

If the temperature has become stationary at each point, a condition of steady flow is established, and $d\theta/dt = 0$. Consequently, the equation of steady flow is

$$\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} = 0,$$

or

$$\nabla^2\theta = 0.$$

In problems where there is spherical symmetry, it is advisable to work in **polar coordinates**. We replace x, y and z by a single variable r, since, from considerations of symmetry, the flow of heat must take place only in the direction of the radius, and the general equation then becomes

$$r^2\frac{\partial\theta}{\partial t} = k\frac{\partial}{\partial r}\left(r^2\frac{\partial\theta}{\partial t}\right).$$

REFERENCES

For more advanced mathematical treatment of problems of heat conduction, see :

Glazebrook, *Dictionary of Applied Physics*, Vol. I, pp. 466-470.
Houstoun, *An Introduction to Mathematical Physics*, pp. 78-108.
Preston, *The Theory of Heat*, pp. 622-649 (1929).
Saha and Srivastava, *A Text Book of Heat*, Chapter VIII.

WORKED EXAMPLES

1. *A long iron rod of diameter 2 cm. is coated with beeswax which melts at a temperature of* 62° *C. If one end is heated to a temperature of* 186° *C., and the wax is melted off for a length of* 15 *cm., calculate the surface emissivity of the rod under the conditions of the experiment.* [*Thermal conductivity of iron* = 0·16 *C.G.S. Centigrade units.*]

We have seen that the differential equation for the flow of heat in a long bar is

$$\frac{d\theta}{dt} = k\frac{d^2\theta}{dx^2} - \mu\theta,$$

where k is the diffusivity, and μ a constant depending on the radiation loss.

For the steady state we have

$$k\frac{d^2\theta}{dx^2} = \mu\theta,$$

and under the conditions of the experiment, which correspond to those of the experiment of Ingenhausz, we have

$$ml = \log_e(\theta_0/\theta_1)$$

where

$$m^2 = \frac{\mu}{k} = \frac{Ep}{KA}.$$

Now, $\theta_0 = 186°$ C., $\theta_1 = 62°$ C., and $l = 15$ cm.;

$$\therefore \; 15m = \log_e(186/62) = \log_e 3 = 1 \cdot 25 \; ;$$

$$\therefore \; m = \frac{1 \cdot 25}{15} = 0 \cdot 0833.$$

Further, $p = $ perimeter $= 2\pi r$ cm.,

                $A = $ area of cross-section $= \pi r^2$ cm.^{2},

and $K = $ thermal conductivity $= 0 \cdot 16$ C.G.S. units.

The radius $r = 1$ cm.,

$$\therefore \; m^2 = \frac{Ep}{KA} = \frac{2E}{0 \cdot 16} \; ;$$

$$\therefore \; E = \tfrac{1}{2}(0 \cdot 16) \times (0 \cdot 0833)^2 = 0 \cdot 00055 \text{ cal. cm.}^{-2} \text{ sec.}^{-1} \text{ °C.}^{-1}.$$

The surface emissivity is, however, a function of the temperature and cannot be regarded as a true physical constant.

2. *At depths of 6, 12, 24 feet the annual ranges of fluctuation of temperature are 5·6° C., 2·8° C., 0·7° C. Find the velocity of propagation of the temperature wave into the earth. Calculate also the diffusivity of the earth's crust.*

The mathematical expression for an infinite train of progressive harmonic waves is

$$y = A \cos 2\pi \left(\frac{t}{\tau} - \frac{x}{\lambda} \right),$$

where λ is the wave-length, that is, the distance between two successive crests at any instant, and τ is the period, that is, the time taken by a complete wave to pass a fixed point.

The velocity of propagation of the wave (V) is thus given by $V = \lambda/\tau$.

In the study of progressive waves it is convenient to use the term **pulsatance,**[*] ω, to represent the number of vibrations in 2π units of time, so that $\omega = 2\pi/\tau$. This quantity corresponds to angular velocity in the reference circle in the customary definition of simple harmonic motion. Such a motion is represented by the equation $y = A \cos \omega t$, where A is the amplitude and ω the pulsatance.

Similarly, in discussing wave motion, it is convenient to introduce a quantity, κ, which may be called the **undulatance,**[†] expressing the number of waves, each of wave-length λ, in 2π units of length, so that $\kappa = 2\pi/\lambda$. The equation for the progressive harmonic wave now becomes

$$y = A \cos (\omega t - \kappa x).$$

The velocity of propagation of the wave (phase velocity) is given by $V = \lambda/\tau = \omega/\kappa$, and thus is obtained by dividing the pulsatance by the undulatance. This follows from the fact that if we substitute $t + t'$ for t, and $x + \dfrac{\omega}{\kappa} t'$ for x, the equation is unchanged in form.

* A. Campbell, *Proc. Phys. Soc.*, Vol. 31, p. 80 (1919).

† H. S. Allen, *Nature*, Vol. 125, p. 561 (1930).

The equation we have derived on p. 706 for a temperature wave is

$$\theta = \iota\, e^{-\sqrt{\frac{\omega}{2k}}\,x} \cos\left(\omega t - \sqrt{\frac{\omega}{2k}}\,x - \epsilon\right);$$

$$\therefore\ V = \omega \left/ \sqrt{\frac{\omega}{2k}} \right. = \sqrt{2\omega k}.$$

The amplitude of the fluctuation at any distance x is given by

$$\theta_0 e^{-\sqrt{\frac{\omega}{2k}}\cdot x} = \theta_0 e^{-bx}, \quad \text{where} \quad b = \sqrt{\frac{\omega}{2k}}.$$

From the data supplied, we have

$$5\cdot 6 = \theta_0 e^{-6b}, \quad 2\cdot 8 = \theta_0 e^{-12b}, \quad 0\cdot 7 = \theta_0 e^{-24b}.$$

Dividing the first equation by the second, we have

$$2 = \frac{e^{-6b}}{e^{-12b}} = e^{6b};$$

$$\therefore\ \log_e 2 = 6b;$$

$$\therefore\ 6b = 0\cdot 69315;$$

$$\therefore\ b = 0\cdot 11552.$$

The same value of b can be obtained from any two of the equations, and this tells us that the wave is being propagated in a regular manner.

We are now in a position to calculate V.

$$V = \sqrt{2\omega k} = \omega\sqrt{\frac{2k}{\omega}} = \frac{\omega}{b}.$$

But the pulsatance $\omega = \dfrac{2\pi}{\tau}$, and in this case the period τ is 365 days;

$$\therefore\ \omega = \frac{2\pi}{365};$$

$$\therefore\ V = \frac{\omega}{b} = \frac{2\pi}{365 \times 0\cdot 1155} = 0\cdot 1491;$$

$$\therefore\ \text{the velocity of propagation is } 0\cdot 15 \text{ feet per day.}$$

We can also calculate the diffusivity k, for since $b = \sqrt{\dfrac{\omega}{2k}}$, we have

$$k = \frac{\omega}{2b^2};$$

$$\therefore\ k = \frac{2\pi}{365 \times 2 \times (0\cdot 1155)^2} = 0\cdot 6453 \text{ sq. ft. per day,}$$

or, expressing this in C.G.S. units,

$$k = 0\cdot 6453 \times \frac{(30\cdot 48)^2}{86400} = 0\cdot 00694 \text{ cm.}^2 \text{ sec.}^{-1}.$$

QUESTIONS

CHAPTER XXXV

1. Establish the differential equation for the flow of heat through a lagged bar of uniform cross-section, heated at one end. If the temperature at the hot end of a long bar is represented by $T_0 \sin pt$, indicate how the thermal conductivity of the material may be determined from temperature observations made at different points of the bar. (L.U., Spec. B.Sc.)

2. A thin rod of uniform cross-sectional area is situated in air at temperature $0°$ C. Obtain the differential equation for the flow of heat in the rod, when the steady state is established. Solve it and indicate a problem to which the solution may be applied. (St. A. U.)

3. Discuss the propagation of temperature waves along (a) a perfectly jacketed, (b) an unjacketed bar.
Give an account of experiments in which the results obtained have been applied to the determination of thermal conductivity. (Camb. Part II Tripos.)

4. Derive an equation for the steady flow of heat along a bar heated at one end and cooled at the other. How will it be modified if heat losses from the sides of the bar are prevented ?
A bar of length 30 cm. and uniform cross-section 5 cm.² consists of two halves, AB of copper and BC of iron, welded together at B. The end A is maintained at 200° C., the end C at 0° C , and the sides are thermally insulated. Find the rate of flow of heat along the bar when the steady state has been reached. [Thermal conductivities are: copper, 0·9; iron, 0·12; in the usual units.] (L.U., B.Sc.)

5. State the Law of Wiedemann and Franz, and describe the method used by these workers to obtain a comparison of the thermal conductivities of metal bars.

6. Find an expression for the temperature at any point along a long bar, surrounded by a non-conducting jacket, if one end of the bar has a periodically varying temperature given by $\theta = \theta_0 \cos wt$.
If the temperature at one end of the bar varies between 15° C. and 45° C. in a complete period of five minutes, to what distance could the variation of temperature be detected by a thermometer reading to $\frac{1}{16}$th of a degree centigrade ?

The thermal conductivity of the metal = ·3 cal./cm /sec./° C.,
the density = 7 gm./c.c.,
and the specific heat = ·1 cal./gm. (E.U., M.A. Hons.)

7. One end of a long uniform bar is maintained at a temperature θ_1 above its surroundings. Show that when a steady state is attained the temperature at any point distance x from the hot end exceeds that of the surroundings by an amount $\theta = \theta_1 e^{-\alpha x}$, where α is a constant for a specified bar. Point out any assumptions made in deducing the equation.
Describe how you would determine α by experiment for a brass rod.
(L.U., B.Sc.)

8. Give some account of the mode of propagation of the annual wave of temperature into the earth and derive an approximate expression for the wavelength in terms of the appropriate thermal and other constants. (L.U., Spec. B.Sc.)

9. Describe the experiments made by Ångstrom on the measurement of the thermal conductivities of metal bars, and explain in what way the simple theory has to be modified under the actual conditions of his experiments.

10. Obtain an equation to represent the steady flow of heat radially outward from a point source in a conducting medium.

CONVECTION

Introduction. We observed in Chapter XVIII when we were considering the transference of heat from one body to another that convection could be described as the process by which heat is transferred in a liquid or a gas in consequence of the actual motion of the heated particles of matter. Since the actual transfer from molecule to molecule takes place by conduction, convection may be regarded as a particular case of the phenomenon of conduction.

In problems relating to the transfer of heat by convection we are, as a rule, concerned with the *rate* at which the heat is transmitted. This **rate of transfer of heat** is also termed the **thermal transmission,** or by some writers the **heat-loss.** It is convenient to have a special symbol for this quantity, and since the letters H and h have been adopted to denote enthalpy or total heat, we shall in this chapter use the symbol $\mathbf{h}$ to denote the quantity of heat transferred from any given body in unit time. This rate may be expressed in any convenient units, such as calories per second or ergs per second.

In certain experiments it is often convenient to deal with the rate at which heat is transferred across unit area, and we shall employ the symbol $\mathbf{h}_A$ to represent the **thermal transmission per unit area,** or the heat transferred across unit area in unit time. In experiments on cylindrical wires it is convenient to deal with unit length of a long wire, and we shall use $\mathbf{h}_L$ for the heat transferred from unit length of the wire in unit time.

A distinction is usually made between two types of convection, natural and forced. In the case of **natural convection,** we have essentially a gravity effect, and the convection currents are produced owing to the differences in density in the body of the fluid itself. For example, if a hot body is situated in air which is at a lower temperature, the air near the surface of the body will be heated and consequently it will rise, since warm air is less dense than cold air. A fresh supply of cold air will be brought in to take its place. This in turn will be warmed, and a definite natural or free convection current will have been formed.

In the case of **forced convection,** the motion of the fluid is brought about by outside forces unconnected with the temperature of the fluid, such as

external pressure differences. An example of this is the case of a hot body which is cooled by means of a steady draught. Forced convection currents are often of much greater magnitude than those due to free convection, and the natural convection effect is often completely obscured.

EXPERIMENTAL INVESTIGATIONS

In the experimental study of convection, almost all the work which has been done has been on the cooling of spheres, flat plates, and cylindrical pipes or wires. This is natural when we consider that these are the types of surfaces most usually met with either in the laboratory or on a large scale in commercial works. Furthermore, since the rate of cooling of a body by convection depends upon the shape of a body, and since the mathematical theory of convectional cooling has only been worked out at present for bodies of simple shape, research workers have usually confined their investigations to those cases where their experimental results can be tested by theoretical calculations.

Natural convection. So long ago as 1817 Dulong and Petit * investigated the loss of heat from thermometer bulbs which were surrounded by a constant temperature enclosure. The heat lost per unit time, **h**, was found to be due both to convection and radiation, but the radiation effect was determined separately by observing the rate of cooling when the enclosure was evacuated. The enclosure was subsequently filled with gas at varying pressures, and the following empirical formula was obtained :

$$\mathbf{h} = mp^{0\cdot45}\theta^{1\cdot233}$$

where m is a coefficient which is different for different gases and depends upon the shape and position of the body, p the pressure of the gas, and θ the temperature difference between the body and its surroundings.

Péclet † investigated the effect that the shape of the hot body exercised on the convectional cooling and obtained the following formulae for the rate of transfer per unit area for the air effect alone :

for a horizontal infinitely long cylinder of brass, $\mathbf{h}_A = 2\cdot058 + \dfrac{0\cdot382}{r}$,

for a sphere, $\mathbf{h}_A = 1\cdot774 + \dfrac{0\cdot13}{r}$,

where r is the radius of the cylinder or sphere, and the units employed are kilocalories, metres and hours. Thus according to Péclet the heat-loss due to convection is not strictly proportional to the area of the

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* Dulong and Petit, *Ann. de Chim. et Phys.*, Vol. 7 (1817). These remarkable experiments on the laws of cooling are described in Preston's *Heat*.

† Péclet, *Traité de la chaleur*, 1860, translated by Paulding. Van Nostrand Co. (1904). See also A. W. Porter, *Phil. Mag.*, Vol. 39, p. 268 (1895).

surface, as is shown by the presence of the term containing r, the radius, in the formula.

The most thorough investigation of the natural convection from flat surfaces has been made by Langmuir.* He used a disk of diameter 19·1 cm., and in order to reduce the radiation effect as much as possible he worked with a surface of highly polished silver. The disk was heated electrically by passing a current through a resistance fastened to the back surface, and the temperature was measured by means of a thermocouple. He worked up to temperatures as high as 600° C., and after the radiation correction had been applied, he obtained the formula

$$h_A = 0 \cdot 0000466 \; \theta^{5/4}$$

for the heat-loss due to natural convection, when the disk was set up vertically. The units employed are calories, centimetres and seconds. He found that the heat-loss was slightly greater than this when the disk was set up horizontally with the face upwards, but considerably less when it was arranged horizontally with the face downwards.

Many experiments † have been made on the natural convection from wires and cylinders. Ayrton and Kilgour ‡ used fine platinum wires of diameter from 0·005 cm. to 0·036 cm., and made the wire serve as its own resistance thermometer for the measurement of temperature up to 600° C. Similar experiments were later made by Langmuir,§ who found agreement with the $\theta^{5/4}$ law up to temperatures of 600° C., but above that found that the index of θ increased from a value of 1·24 at low temperatures to 1·53 at 1430° C. He explained this on the theory that there is a stationary film of gas of definite thickness in contact with any object even at high temperatures. He maintained that free convection consists essentially of conduction through this film and that the heat-loss can be calculated from the ordinary laws of conduction.

Forced convection. The study of the heat-loss from a vertical flat plate when cooled by a steady draught of air has been studied by Jürges.|| He used a square copper plate, of side 50 cm., whose temperature was maintained electrically. The velocity of the air was measured by means

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* Langmuir, *Trans. Amer. Electrochem. Soc.*, Vol. 23, p. 299 (1913).

† A full bibliography of the whole subject of convection both natural and forced, together with a summary of the principal experimental work, will be found in *The Calculation of Heat Transmission*, Fishenden and Saunders. H.M. Stationery Office (1932).

‡ Ayrton and Kilgour, *Phil. Trans. Roy. Soc.*, A, Vol. 183, p. 371 (1892).

§ Langmuir, *Phys. Rev.*, Vol. 34, p. 401 (1912).

|| Jürges, *Beihefte zum Gesundheits-Ingenieur*, Reihe I, Heft 19 (1924).

of a Pitot tube,* and he found the relation between rate of loss of heat per unit area h_A, and velocity V was given by $h_A = a + bV$ for velocities not exceeding 50 cm. sec.$^{-1}$, and $h_A = cV^{0.78}$ for velocities above this value, a, b and c being appropriate constants. In both cases the heat-loss was proportional to the temperature difference between the plate and the . steady draught.

For the case of a cylinder at right angles to the cooling stream, the work of Hughes † on large cylinders, and King ‡ on fine wires, must be mentioned. Hughes worked with hollow cylinders of diameter (d) 0·43 to 15·5 cm. through which steam could be passed. The heat-loss was measured by the amount of steam that was condensed, and the wind velocity V by a Pitot tube. He found that the heat-loss h_L was proportional to $\theta\, d^m V^n$, where m has a value of 0·57 and n varies from 0·55 for small diameters to nearly 1·0 for large diameters.

King worked with fine platinum wires of diameters from 0·015 to 0·003 cm. He mounted them on a rotating arm capable of adjustment over a range of velocities from 17 to 900 cm. per sec. The resistance of these wires was determined by the Kelvin double bridge system, and the temperature of the wire both at rest and when in motion was calculated from a knowledge of the resistance and the temperature coefficient of the particular sample of platinum. The temperature difference between the wire and the surrounding air ranged from 200° to 1200° C.

King carried out a very large number of experiments and obtained excellent agreement with his theoretical calculations. He obtained for unit length of wire the relation

$$h_L = \theta(B\sqrt{Vd} + C),$$

where B and C are constants and the other symbols have the usual meanings. This expression is only valid when Vd exceeds a certain value, which under the conditions of his experiments was 0·0187. Below this value, i.e. for very low velocities or for very thin wires, another and more complicated relationship was obtained. Natural convection probably plays a large part in the heat loss for these very low velocities, and needs to be taken into account in any theoretical consideration.

Turbulent flow. Most of the work which has been done on forced convection has been confined to streamline flow, but Osborne Reynolds § has investigated the case of turbulence. He states that in this case

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* The Pitot tube is a device for determining the velocity of a fluid at a given point by measuring the pressure set up in an open-mouthed tube facing the current. See *Dict. App. Physics*, Vol. I, p. 351.

† Hughes, *Phil. Mag.*, Vol. 31, p. 118 (1916).

‡ King, *Phil. Trans. Roy. Soc.*, Vol. 214, p. 373 (1914).

§ Reynolds, *Proc. Lit. Phil. Soc. Manchester*, Vol. 14, p. 9 (1874).

convection is due to two causes, namely, natural internal diffusion and the visible eddy motion which mixes the fluid up and continually brings fresh particles into contact with the surface. He gives the formula for the heat-loss **h** as $\mathbf{h} = (A + B\rho V)\theta$, where A and B are constants and V and ρ are the velocity and density of the fluid.

THEORETICAL INVESTIGATIONS

The mathematical treatment of both natural and forced convection presents great difficulty. The general equations which govern the motion of a fluid possessing convection currents can usually be established, but the application to actual problems has not met with success, except in a few of the simpler cases. This failure is principally due to the simplifying assumptions, that have to be made in order to solve the theoretical problem, not being valid in actual experience.

Lorentz * investigated the heat-loss $\mathbf{h}_A$ due to natural convection from a vertical surface freely exposed to air, and found that $\mathbf{h}_A \propto \theta^{5/4}$, where θ is the temperature difference between the surface and the air.

In the realm of forced convection, Boussinesq † has investigated the cooling of a hot body by a stream of fluid when the flow is not turbulent, and he obtained a generalised solution in which he showed that the rate of loss of heat was directly proportional to the temperature difference between the body and the fluid. He also solved certain particular cases, notably that of a cylinder or wire with its axis at right angles to the direction of flow, and found that the rate of loss of heat $\mathbf{h}_L$ was given by

$$\mathbf{h}_L = A\theta\sqrt{Vd},$$

where θ is the temperature excess of the wire over its surroundings, V the velocity of the stream, d the diameter of the wire, and A is a constant depending upon the physical properties of the fluid.

King carried Boussinesq's analysis still further and found the relation

$$\mathbf{h}_L = \theta(B\sqrt{Vd} + C)$$

for the rate of loss per unit length due to forced convection from cylindrical wires, and obtained satisfactory experimental confirmation of his formula as has already been described above.

Principle of similitude. The theoretical treatment of convection is probably most easily dealt with by the principle of similitude. The essence of this is that phenomena themselves do not depend upon the units in which we measure them. Rayleigh ‡ has applied this principle

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* Lorentz, *Ann. der Phys.*, Vol. 13, p. 582 (1881).

† Boussinesq, *Comptes Rendus*, Vol. 133, p. 257 (1901) ; also, *Journal de Mathématiques*, Vol. 1, p. 285 (1905).

‡ Rayleigh, *Nature*, Vol 95, p. 66 (1915). See also A. W. Porter, *The Method of Dimensions*, Chapter 5 (1933).

to forced convection in the case of a steady flow of heat from a good conductor immersed in a stream of incompressible fluid moving (at a distance from the solid) with a velocity v. First of all he considered the simple case when the viscosity of the fluid is ignored. He then postulated that the quantity of heat h passing in unit time is a function of the following quantities, whose dimensions with respect to mass, length, time and temperature are shown in the table below. Heat is regarded as having the dimensions of energy ML^2T^{-2}.

Quantity	Symbol	Dimensions
Linear dimensions of the body - -	l	L
Temperature difference between fluid and surface of solid - - - -	θ	Θ
Velocity of the fluid at a distance from the solid - - - - - -	V	LT^{-1}
Heat capacity of fluid per unit volume -	C	$ML^{-1}T^{-2}\Theta^{-1}$
Thermal conductivity of the fluid - -	K	$MLT^{-3}\Theta^{-1}$

We may now write down arbitrary indices for these quantities, and express them in the form of the equation

$$\mathbf{h} = l^v \theta^w V^x C^y K^z.$$

We know further that h, the heat passing in unit time, possesses dimensions ML^2T^{-3}, and by equating the coefficients of the dimensional equation, we find

$$\text{by mass,} \qquad 1 = y + z;$$
$$\text{by length,} \qquad 2 = v + x - y + z;$$
$$\text{by time,} \qquad -3 = -x - 2y - 3z;$$
$$\text{by temperature,} \quad 0 = w - y - z.$$

This gives us four equations and five unknown quantities. Therefore we cannot find all of the values, but if we solve the equations in terms of one of the unknowns (say x), we find

$$v = 1 + x,$$
$$w = 1,$$
$$y = x,$$
$$z = 1 - x.$$

If we now substitute these values in the dimensional equation and collect the indices, we obtain the result

$$1 = Kl\theta \left(\frac{VCl}{K}\right)^x.$$

Since x is undetermined, and $\dfrac{VCl}{K}$ is of zero dimensions, any number of terms of this form may be combined, and all that we can conclude is that

$$\mathbf{h} = Kl\theta F\left(\frac{VCl}{K}\right),$$

where F is an arbitrary function of $\dfrac{VCl}{K}$.

This equation agrees with Boussinesq's general solution.

Rayleigh then went on to examine the effect that the viscosity of the fluid (ν) has on the dimensional equation. Viscosity has dimensions (L^2T^{-1}), and if a factor ν^u is introduced, the equation is reduced to the form

$$\mathbf{h} = Kl\theta\left(\frac{VCl}{K}\right)^x\left(\frac{C\nu}{K}\right)^u,$$

where x and u are both undetermined.

As before, we may write

$$\mathbf{h} = Kl\theta F\left(\frac{VCl}{K}, \frac{C\nu}{K}\right)$$

This last factor, $\dfrac{C\nu}{K}$, appears to be constant for a given kind of gas, and only varies moderately from one kind to another. If this may be regarded as true, then the expression for the rate of loss of heat $\mathbf{h}$ reduces to the same expression as in the case where the viscosity was neglected. Thus, in any case, viscosity appears to have less effect than might have been anticipated.

We can simplify this result still further when we consider a cylinder such as a wire, of diameter d, and with its long axis perpendicular to the direction of flow. The form of the first function then becomes $\dfrac{VCd}{K}$, but since we already know that $\dfrac{C\nu}{K}$ is a constant, we may write the equation in the form

$$\mathbf{h} = Kl\theta F\left(\frac{Vd}{\nu}\right).$$

The quantity $\dfrac{Vd}{\nu}$, known as the Reynolds's number, is of great importance in hydrodynamics and is continually met with in experiments on fluid resistance and flow.

The equation arrived at above has been used by Davis [*] to compare experimental results obtained by different workers. Fig. 262 shows a remarkable agreement over a range which extends from steam pipes of 5 cm. diameter down to the very fine platinum wires of 0·003 cm. used by King,[†] when $\mathbf{h}_L$ (or H in the diagram) is plotted against Vd.

[*] Davis, *Phil. Mag.*, Vol. 40, p. 692 (1920).   [†] King, *loc. cit.*

Davis * and L. F. Richardson † have also applied the principle of similitude to the case of natural convection, and a relation

$$\mathbf{h} = K\theta l F\left(\frac{C^2 A\theta l^3}{K^2}\right)$$

has been obtained, where A is of dimensions $LT'^2\theta^{-1}$, and depends upon the acceleration of the convection currents. The other symbols possess the same meaning as before.
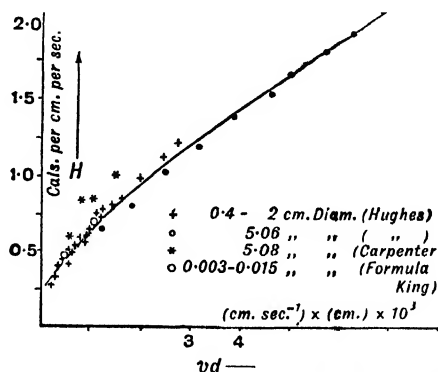
FIG. 262. COMPARISON OF CONVECTION EXPERIMENTS BY MEANS OF THE PRINCIPLE OF SIMILITUDE

As has already been stated, there is considerable evidence, both theoretical and practical, that $\mathbf{h} \propto \theta^{\frac{5}{4}}$. If this is the case, the functional equation reduces to

$$\mathbf{h} \propto K^{-\frac{1}{2}}\theta^{\frac{5}{4}}l^{\frac{7}{4}}C^{\frac{1}{2}}A^{\frac{1}{4}}.$$

APPLICATIONS OF CONVECTION

The convectional cooling of hot wires has met with several practical applications, among which may be mentioned the hot wire anemometer and the hot wire microphone.

The hot wire anemometer. If we know the relationship between the cooling of a hot wire and the velocity of the draught of air which brings about that cooling, it at once follows that an instrument for the measurement of wind velocities can be constructed on these lines. King ‡ and Morris § have both designed such instruments, while Thomas ‖ has also made many similar experiments on the flow of gases in pipes.

This method of hot wire anemometry has been modified and used by

* Davis, *loc. cit.*

† L. F. Richardson, *Proc. Phys. Soc.*, Vol. 32, p. 405 (1920).

‡ King, *ibid.*

§ Morris, *Brit. Ass.* 1912, *Electrician*, Oct. 4, 1912, *Engineering*, Dec. 27, 1912.

‖ Thomas, *Phil. Mag.*, Vol. 39, p. 505 (1920).

E. G. Richardson * for the measurement of the amplitude of sound waves in pipes.

The hot wire microphone. This instrument was developed in war time by Tucker and Paris † for the detection of the sounds produced by the firing of heavy guns, and was utilised for various methods of determining the positions of concealed batteries by means of sound ranging. The instrument consists of a fine platinum wire grid of diameter 0·0006 cm. which is mounted in a circular mica plate, and the whole is fixed in the neck of a large resonator. The grid is heated electrically until it is red-hot, and when it is exposed to a train of sound waves, these waves cool it and lower its electrical resistance.

Two effects are produced in consequence of this cooling : (1) a fall of resistance by a constant amount proportional to the intensity of the sound, that is, proportional to the square of the amplitude of the wave, and (2) an oscillatory change of resistance proportional to the amplitude of the sound wave. These effects can be observed experimentally in two ways : (1) the steady resistance drop may be measured in a Wheatstone bridge network, and (2) the potential variations due to the periodic change of resistance can be amplified and observed by means of a vibration galvanometer.

QUESTIONS

CHAPTER XXXVI

1. Describe the phenomenon of convection
What do you understand by the terms *free convection* and *forced convection* ?

2. Describe any experiments which tend to show that the rate of loss of heat from a body is proportional to the five-fourths power of the temperature excess between the body and its surroundings.

3. Discuss the heat-loss from cylindrical bodies which are cooled by a draught of air of known velocity.

4. What do you understand by *the principle of similitude* ? Describe any physical problem which has been solved by this means.

5. Describe any practical applications of convection which have proved of service in the design of scientific instruments.

6. Describe an experiment to measure the heat-losses due to convection from a plate, at various pressures of the surrounding gas. Give a diagram.

(L.U., B.Sc. Special.)

* E. G. Richardson, *Proc. Roy. Soc.*, A, Vol. 112, p. 522 (1926).

† Tucker and Paris, *Phil. Trans. Roy Soc.*, A, Vol. 221, p. 389 (1921).

CHAPTER XXXVII

THE MEASUREMENT OF RADIATION

The earlier methods of measuring radiant energy have already been described (Chapter XX), and we shall now consider in greater detail the more accurate methods and the instruments employed. Subsequently an account will be given of some of the applications of these methods.

RADIOMETERS

THE word **radiometer** was first used by Sir William Crookes to describe an instrument (p. 401) illustrating the transformation of radiant energy into mechanical energy of rotation (1875). It is now often used in a more general sense to denote any instrument for the measurement of radiation.

1. THE BOLOMETER

Langley's bolometer. About the year 1881, the platinum resistance thermometer was modified by Langley in America, in order to produce a very sensitive instrument for the detection of thermal radiation. A fine strip of metal is exposed to the source of radiation by opening a narrow slit placed parallel to the strip. The electrical resistance of the metal strip changes as its temperature changes, and by means of a Wheatstone bridge we can measure this change in resistance. Langley used platinum, steel, and palladium in his experiments, but at the present time platinum is generally used. Sensitivity was obtained by constructing a grating punched from a thin sheet of metal foil, this grid being very similar in form to that shown in Fig. 264. The surface was blackened so that it might absorb as much radiation as possible. Such an instrument is known as a **bolometer.**

Langley used two exactly similar platinum grids, which formed two arms of the Wheatstone bridge. One of these grids is exposed to the radiation, and the other one is shielded by enclosing it in a suitable case. By using the grids differentially in this way, any temperature change in the room will affect both sides of the bridge equally, and consequently the balance of the circuit will not be upset. The exposed grating must

be enclosed in a copper-lined chamber in order to secure equable temperature distribution.

The bridge is at first balanced when both grids are screened from the source of radiation. Then radiation is allowed to fall on one of the grids, and owing to the change in resistance, the Wheatstone network is thrown out of balance. This causes a measurable deflection of a sensitive galvanometer, and Langley found that with his apparatus he could measure changes in temperature as low as $10^{-4}\,^{\circ}$C.

One advantage of the bolometer is that there is very little time lag, because the metal strips are so thin that they take up and part with heat almost instantaneously.

The bolometer of Lummer and Kurlbaum. In the bolometer constructed by Lummer and Kurlbaum several improvements are introduced. Four grids are used ; one is placed in each arm of the Wheatstone bridge, and the circuit is connected up as shown in Fig. 263. The
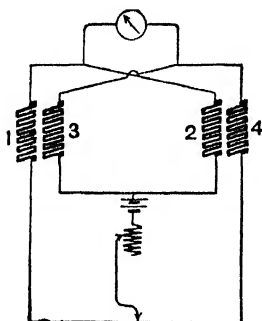
FIG. 263. ELECTRICAL CONNECTIONS FOR LUMMER-KURLBAUM BOLOMETER
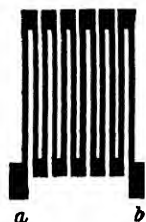
FIG. 264. GRID OF LUMMER-KURLBAUM BOLOMETER

advantage of this method is twofold : (1) Temperature changes in the apparatus are completely compensated, and (2) the effect due to the radiation is doubled because the two gratings belonging to opposite arms of the bridge are placed immediately behind one another, so that the strips of the one cover the gaps of the other.

The grids are constructed in the shape shown in Fig. 264, and have a resistance of about 60 ohms each. The platinum foil is only 0·0005 mm. in thickness, and it is covered with platinum black, so that it becomes an efficient absorber of heat. The whole apparatus, which is shown in Fig. 265, is enclosed in a well lagged box. This is provided with diaphragms which cut down the radiation falling on the grids to a parallel beam of diameter about 16 mm. An accuracy of about 0·01 per cent. is claimed for this type of bolometer.

Such an instrument has also been employed to detect Hertzian waves and in the measurement of dielectric constants.
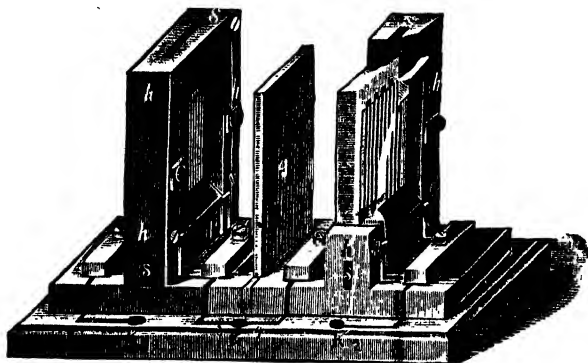
FIG. 265. LUMMER-KURLBAUM BOLOMETER

2. THE RADIOMICROMETER

The radiomicrometer of Boys. Professor C. V. Boys, who has shown extraordinary skill in the design and construction of sensitive apparatus, in 1888 turned his attention to the problem of measuring very small amounts of radiation. He devised an instrument, which he called the **radiomicrometer,** based on the principle of the thermocouple. In the thermopile the electromotive force produced (for a given difference of temperature between the opposite faces of the pile) is proportional to the number of junctions, but it must be remembered that an increase in this number is accompanied by a corresponding increase in resistance. Boys solved the problem of detecting the current in a single couple and by diminishing the number of elements greatly reduced the mass of the part to be heated.

FIG. 266. BOYS'S RADIOMICROMETER

The radiomicrometer (Fig. 266) contains

two elements only, a small bar of antimony and a small bar of bismuth placed side by side. The lower ends of these bars are joined to a circular disk of thin copper which is blackened so as to absorb radiation falling upon it. The upper ends of the bars are connected by a small loop of fine bare copper wire ; this in turn is attached to the lower end of a very fine glass capillary tube which is suspended by means of a fine quartz fibre.

A very light galvanometer mirror is fastened to the capillary tube. The copper loop is in a gap between the poles of a strong magnet NS, but the little bars of antimony and bismuth hang below in a space hollowed out in a block of soft iron ; they are thus screened from any magnetic effect. When radiation falls upon the copper disk through the horizontal aperture, the lower junction is heated and consequently an electric current travels round the circuit. Since the copper loop is in a magnetic field, the suspended system tends to turn about a vertical axis, this tendency being opposed by the couple due to the suspending fibre. The arrangement in fact constitutes a moving-coil galvanometer. The moving part is very small, and as the circuit is short the electric resistance is also small, and the thermoelectromotive force of a single couple can drive a current round the circuit sufficient to cause a measurable deflection.

The radio-micrometer possesses many advantages. It is very sensitive, and is quick in action ; the zero is constant, and does not " creep ". Further, it is uninfluenced by outside thermal or magnetic effects ; indeed, a strong magnet may be moved about quite near to the instrument without disturbing it. The sensitivity can be varied at will, and if it is desired to use the instrument in spectroscopic work, the radiation may be limited by means of a narrow slit without decreasing the sensitivity unduly. The sensitivity is so great that the radiation received by the mirror of a reflecting telescope of 16 inches aperture from a candle at a distance of between two and three miles has been detected by Boys.

The chief disadvantage of the radiomicrometer lies in the fact that it can only be used to receive radiation in a horizontal fixed direction ; in this respect it is less convenient than a bolometer.

3. The Torsion Radiometer

The torsion radiometer of Nichols. The radiometer or " light mill " was invented by Sir William Crookes about 1875. A number of vanes are mounted so as to be able to turn about a vertical axis, each vane having one face polished and one face blackened. When such a light mill is exposed to a sufficiently intense source of radiation, the vanes are set in rotation and the rate of rotation increases with the intensity of the radiation. The theory of the action has been discussed in Chapter XVIII, p. 401. The temperature of the blackened face which absorbs radiation is raised above the temperature of the polished face, and rotation is due

to the difference in the resulting velocity of the gaseous molecules striking the faces. E. F. Nichols suspended the vanes by a fine quartz fibre, and so constructed what may be called a **torsion radiometer** (Fig. 267). In this improved radiometer we do not get continuous rotation of the suspended system, but the vanes, $V_1 V_2$, turn through a definite angle depending on the intensity of the radiation falling upon them through the window, CC. There is in fact a balance between two effects, the couple arising from the action of radiation being balanced by the couple arising from the torsion of the fibre, F. By attaching a small mirror, M, to the suspended system we can measure the angle of deflection, using a lamp and scale.
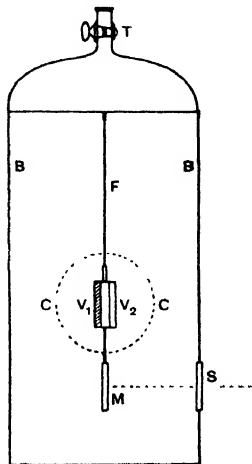
B = case of instrument.
F = torsion fibre.
M = mirror.
C = window to admit radiation.
T = tap for exhausting apparatus.
$V_1 V_2$
S = window to admit light for scale.

FIG. 267. TORSION RADIOMETER
OF NICHOLS

Comparison of different types of instruments. These different instruments have been compared with one another, and it has been found that when a constant source of radiation is used the torsion radiometer is the most sensitive of all, particularly in the infrared regions of the spectrum. It should be used, *provided that the source of radiation is constant.* The radiomicrometer of Professor Boys does not reach more than about $\frac{1}{8}$th part of the sensitiveness of the bolometer, but Nichols * claims that his radiometer is 12 times as sensitive as the radiomicrometer of Boys.

Great improvements have also been made in the construction of the linear thermopile within recent years, and modern thermopiles vie with these other instruments in measuring accurately small quantities of radiation.

Two other modern instruments deserve mention : **photoelectric cells, and selenium cells.** In a modern photoelectric cell a surface of sodium or caesium is exposed to the radiation, and, in a high vacuum, electrons are emitted from the surface. The stream of electrons constitutes an electric current, and by employing suitable electric methods the current may be measured and serves to give an estimate of the radiation falling upon the cell. In the case of the selenium cell, radiation has the effect of changing the electrical resistance, and in this apparatus also electrical methods are used to detect this change of resistance. These are ex-

tremely sensitive methods, especially when valve amplifiers are used to magnify the current produced, but both the instruments are selective, and are unsuitable for the measurement of thermal radiation when the wave-length lies in the infra-red region.

PRESSURE OF RADIATION

According to the corpuscular theory of light we should expect the rapidly moving corpuscles to exert an effect equivalent to a pressure on any surface on which light falls. The change in momentum when a corpuscle is stopped or reflected may be attributed to a force exerted by the body on the corpuscle, and the corresponding reaction on the body is a force tending to move it in the opposite direction. The average effect due to a large number of corpuscles may be regarded as a pressure on the surface.

Such an action follows not only from the emission theory of light but also from Clerk Maxwell's electromagnetic theory, and indeed from any form of the undulatory theory. Maxwell calculated the mean pressure in strong sunlight as equivalent to 0·4 milligrams per square metre on a black surface and twice this amount on a perfect reflector. He suggested (1881) that by allowing the concentrated rays of an electric arc lamp to fall on a thin metallic disk, delicately suspended in a vacuum, an observable effect might be detected.

It can be proved by means of the electromagnetic theory that Maxwell's radiation pressure is closely related to the energy of the radiation, but the direct proof is long and somewhat complicated.* A simpler proof given by Larmor,† and known as Larmor's indirect pressure theorem, is discussed below. It is based on general considerations of the propagation of wave motion, and states that the pressure of diffuse radiation falling normally on a surface is equal to one-third of the energy density.

Larmor's indirect pressure theorem.‡ Consider a wave train travelling along the x-axis from $x = \infty$ to $x = -\infty$; its displacement may be written

$$\xi = a \cos 2\pi \left(\frac{x}{\lambda} + \frac{t}{\tau} \right),$$

where λ is the wave-length, τ the period, and its velocity $c = \lambda/\tau$ (see p. 711).

Let this wave train meet a perfectly reflecting surface travelling in the opposite direction with a velocity u. Then at any time t this surface will be in a position given by $x = ut$.

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* See, for example, Planck, *Warmstrahlung*, Part II, Chapter I. English translation by Masius, *The Theory of Heat Radiation* (1914).

† Larmor, *Encyclopædia Britannica*, Vol. 32, Article on " Radiation ".

‡ This section may be omitted at the first reading.

The reflected wave train will have a displacement given by

$$\xi' = a' \cos 2\pi \left(\frac{x}{\lambda'} - \frac{t}{\tau'} \right);$$

$$\therefore \ \xi + \xi' = a \cos 2\pi \left(\frac{x}{\lambda} + \frac{t}{\tau} \right) + a' \cos 2\pi \left(\frac{x}{\lambda'} - \frac{t}{\tau'} \right);$$

and this equation must hold for all values of x and t.

The disturbance is perfectly reflected at the surface and consequently is completely annulled, for it does not travel into the reflector. Therefore when $x = ut$, $\xi + \xi' = 0$.

$$\therefore \ a = -a',$$

and
$$\frac{x}{\lambda} + \frac{t}{\tau} = -\left(\frac{x}{\lambda'} - \frac{t}{\tau'} \right);$$

$$\therefore \ \frac{ut}{\lambda} + \frac{ct}{\lambda} = -\left(\frac{ut}{\lambda'} - \frac{ct}{\lambda'} \right);$$

$$\therefore \ \frac{c+u}{\lambda} = \frac{c-u}{\lambda'};$$

$$\therefore \ \frac{\lambda'}{\lambda} = \frac{c-u}{c+u}.$$

Thus the reflected wave-length is shortened in this ratio.

We now proceed to calculate the **energy density**, that is, the energy per unit volume of the incident and reflected wave trains; let these be denoted by E_1 and E_2 respectively.

Consider unit cross-section and unit length of the incident wave; the kinetic energy of this $= \frac{1}{2}\rho(d\xi/dt)^2$, where ρ is the density.

Now
$$\frac{d\xi}{dt} = -a \times \frac{2\pi}{\tau} \sin 2\pi \left(\frac{x}{\lambda} + \frac{t}{\tau} \right) = -a \times \frac{2\pi c}{\lambda} \sin 2\pi \left(\frac{x}{\lambda} + \frac{t}{\tau} \right);$$

$$\therefore \ \frac{1}{2}\rho \left(\frac{d\xi}{dt} \right)^2 = \frac{2a^2\rho\pi^2c^2}{\lambda^2} \sin^2 2\pi \left(\frac{x}{\lambda} + \frac{t}{\tau} \right).$$

Since the sum of the potential and kinetic energies is constant, the maximum value of this expression, namely $2a^2\rho\pi^2c^2/\lambda^2$, gives E_1 the total **energy per unit length of the wave of unit cross-section.**

Thus the energy of either wave train is inversely proportional to the square of its wave-length, and we have

$$\frac{E_2}{E_1} = \frac{\lambda^2}{\lambda'^2} = \frac{(c+u)^2}{(c-u)^2}.$$

Now let us introduce the conception of **activity** (A) defined as energy per unit time.

For the incident wave train, the activity with reference to a point moving with the reflecting surface equals the energy per unit time passing the point, and we may write

$$A_1 = E_1 \times (c+u).$$

In the same way, for the reflected wave train, we have

$$A_2 = E_2 \times (c - u).$$

$$\therefore \frac{A_2}{A_1} = \frac{E_2}{E_1} \times \frac{c-u}{c+u} = \frac{(c+u)^2}{(c-u)^2} \times \frac{(c-u)}{(c+u)} = \frac{c+u}{c-u}.$$

$$\therefore \frac{A_2 - A_1}{A_1} = \frac{c + u - (c - u)}{c - u};$$

$$\therefore A_2 - A_1 = \frac{2u}{c-u} A_1.$$

Now, this difference in activity must be equal to the work done per second by the advancing reflector against the pressure (P) due to the radiation, and this is equal to the pressure multiplied by the velocity.

$$\therefore A_2 - A_1 = P \times u.$$

Equating these two values for $A_2 - A_1$, we find

$$P = \frac{2}{c-u} \times A_1.$$

We must now turn this into an expression in terms of the energies.

Since

$$\frac{E_1 + E_2}{E_1} = \left(1 + \frac{(c+u)^2}{(c-u)^2} \right) = \frac{2(c^2 + u^2)}{(c-u)^2},$$

remembering that $A_1 = E_1 \times (c + u)$, we may write

$$E_1 + E_2 = \frac{2(c^2 + u^2)}{(c-u)^2} \times \frac{A_1}{c+u}$$

$$= \frac{2(c^2 + u^2)}{(c-u)^2} \times \frac{(c-u)}{2(c+u)} \times P$$

$$= \frac{c^2 + u^2}{c^2 - u^2} P.$$

We have thus found a relation between P and $E_1 + E_2$.

If u is very small compared with c, this expression reduces to

$$P = E_1 + E_2,$$

and therefore the pressure on the reflector is equal to the total energy per unit volume of both the incident and reflected waves.

If now we consider a cube filled with diffuse radiation from an infinitesimal speck of matter so that the energy density is E, then (on analogy with the theory of molecular pressure given in Chapter XIV in connection with the Kinetic Theory of Gases) the pressure due to the radiation incident in all directions and exerted normally *on any one face* of the cube will be given by

$$P = \tfrac{1}{3}E.$$

Experimental investigations of Lebedew and Nichols and Hull on the pressure of radiation. Many attempts were made to detect the pressure due to light falling on a material body, but for a long period the effect could not be disentangled from the " radiometric action " due to the reaction of gas molecules.

The first successful attempt was made in 1900 by Lebedew of Moscow, and shortly afterwards an independent investigation by Nichols and Hull gave more reliable results.

Lebedew to a considerable extent eliminated the radiometric action by using a large bulb with high exhaustion and by excluding rays capable of heating the walls of the tube (Fig. 268). The radiometer vanes were constructed of very thin metal foil, attached to a thin glass rod R, which was suspended by a fine glass fibre F. P_1P_1' were two platinum disks 0·1 mm. thick, and P_2P_2' two similar disks of thickness 0·02 mm. The disks on the left of the diagram (P_1P_2) were polished on both sides so as to reflect all radiation falling on them, while those on the right ($P_1'P_2'$) were blackened on both sides so that they would act as good absorbers. A mirror M was attached to the glass rod so that the deflection could be measured.
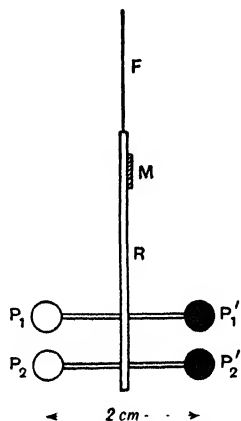
FIG. 268. APPARATUS OF LEBEDEW FOR DEMONSTRATING THE PRESSURE OF RADIATION

The apparatus by means of which Nichols and Hull investigated the pressure of light was arranged as a torsion balance, in such a way that the disturbing actions could in large measure be reversed.* The ballistic method was used on account of the fact that the light pressure acts instantaneously, whereas the gas pressure effect takes some seconds to reach a maximum. By suitably adjusting the pressure of the air in the chamber the gas action was reduced to a minimum.

These experiments provided a quantitative verification of the prediction of Maxwell that the pressure in dynes per sq. cm. is equal to the energy in ergs contained in unit volume (1 c.c.) of the radiation.

PYROMETERS DEPENDING ON THE EMISSION OF RADIATION

The temperature of a luminous body can be roughly estimated from its colour, and the colour is independent of the material of which the

* Nichols and Hull, *Proc. Amer. Acad.*, Vol. 38 (1903) ; see also R. W. Wood, *Physical Optics* (Macmillan).

hot body is composed. Table 51 shows the relationship between the temperature of a furnace and the colour of the light emitted.

TABLE 51

RELATION OF COLOUR TO TEMPERATURE

Colour	Approximate temperature in ° C.
Red (just visible) -	500
Dull red - -	700
Cherry red - -	900
Orange - - -	1100
White - - -	1300
Dazzling white -	1500

These figures must be regarded as approximate, but, as we shall see below, it is possible to obtain accurate comparisons by heating a platinum wire and comparing the colour of the wire (the temperature of which is found by measurement of its resistance) with the colour of the light from the furnace.

In the measurement of high temperatures a study of the radiation emitted provides more than one method for making exact determinations. We may examine the total radiation emitted, including the whole range of wave-lengths, or alternatively we may pay attention to the colour of the radiation. Thus **radiation pyrometry** includes two types of instruments which may be called **total radiation pyrometers** and **optical pyrometers.**

1. TOTAL RADIATION PYROMETERS

Let E be the energy of the total radiation, that is to say, radiation of all wave-lengths, emitted by a black body at absolute temperature T.

Black body radiation. Since we shall have occasion to refer to the term frequently in this and the following sections, we may state again that a **full radiator,** or a **black body,** is one that will completely absorb all the radiation, of whatever wave-length, falling on it. It will neither transmit nor reflect any of the incident radiation. No known substance possesses strictly this property—untreated carbon is probably the nearest approach that can be found to it—but Kirchhoff, about the year 1858, showed that a hollow cavity having its walls at a uniform temperature possesses the properties of a " black body ". The radiation emitted from a small hole in such a body may be termed **black body radiation.** It will depend only upon *the temperature of the enclosure,* and not at all on the substances of which it is composed, or which may be inside it.

For a black body, Stefan's law (see p. 451) states that $E \propto T^4$. This law has been verified experimentally by Lummer and Pringsheim up to 1300° C., and by Mendenhall and Forsythe at 1063° C. and 1549° C., the melting points of gold and palladium respectively. The experimental details of this verification will be described in the next chapter (pp. 746-747) ; this section will deal only with the application of such methods to the measurement of high temperatures.

Féry's total radiation pyrometer. A standard form of **total radiation pyrometer,** designed by Féry, is illustrated in Fig. 269 (a). The radiation

Out of focus

(b)

In focus

(c)
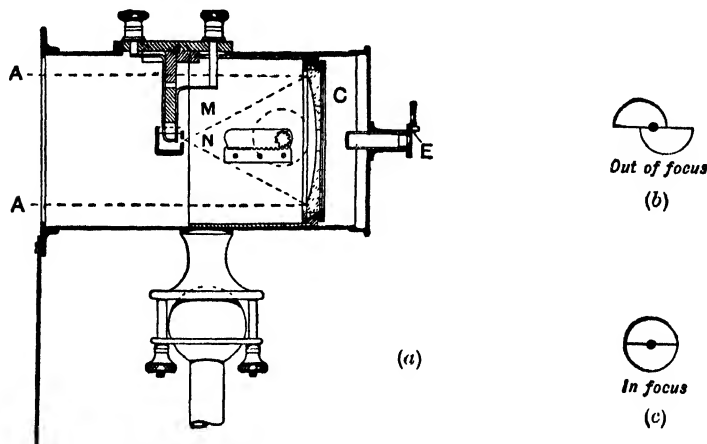
FIG. 269. FÉRY'S TOTAL RADIATION PYROMETER

from the source is received across AA, and, by means of a concave mirror C silvered on its front surface, is focused on one of the junctions of a thermocouple N. N is then said to be the hot junction. The cold junction is shielded from the direct radiation by means of a tongue and a box M. The leads from the thermocouple are joined to a millivoltmeter, and the electromotive force developed is thus determined. It is important to ensure that all the heat rays entering the instrument shall be accurately focused on to the hot junction. In order to effect this the concave mirror is mounted on a rack and pinion device which can be suitably adjusted. Two semicircular mirrors inclined to one another at an angle of 5° to 10° are mounted on the shield M, and an opening of about 1·5 mm. at the centre of the mirrors forms a diaphragm through which the radiation passes on to the hot junction. The furnace is viewed through the eyepiece E, and unless the concave mirror is accurately focused on the thermocouple, the image will appear distorted on account of the inclined mirrors. This is shown in the insert diagram (b). When the apparatus is correctly adjusted, the image will appear as in (c).

If the diaphragm in M is completely filled with the radiation from the source, the reading of the pyrometer is independent of its distance from the furnace. This result can easily be deduced theoretically. Let the distance between the instrument and the furnace be doubled. Then the total amount of heat received by the concave mirror is reduced to one-fourth. But at the same time the area which the image covers is also reduced to one-fourth. Consequently the actual heat intensity of the image measured by the apparatus remains constant, and the reading of the millivoltmeter is unchanged.

In actual practice the relation between the electromotive force of the thermocouple (V) and temperature is $V = a(T^b - T_1{}^b)$, where T and T_1 are the absolute temperatures of the source, and the receiver M, a and b are constants depending upon the actual instrument, and b, which theoretically should equal 4·0, is found to vary between the limits 3·8 and 4·2. The principal reasons which cause b to vary may be summarised as follows : *

(1) The electromotive force produced by the thermocouple is not strictly proportional to the temperature difference between the hot and cold junctions.

(2) Stray reflections from the shielding box M introduce errors.

(3) The conduction of heat along the wires of the thermocouple causes a slight rise in temperature at the cold junction.

(4) The rate of heat loss from the hot junction is not strictly proportional to the temperature excess.

(5) The readings of the millivoltmeter are liable to various errors.

If the temperature of the source is very great, T_1 may be neglected in comparison with T.

Other types of radiation pyrometers. Féry introduced a modification of his mirror pyrometer with a view to making it more robust and more suitable to works conditions. In this form of the instrument the thermocouple is replaced by a bimetallic spring spiral to which is attached an aluminium pointer which moves over a scale graduated directly in degrees. The spiral is of a similar construction to that used in the Dekhotinsky thermoregulator, described in Chapter IV, p. 117, in connection with thermostats. The radiation is concentrated on the spiral by means of the concave mirror, and the resulting rise in temperature causes the expansion which is indicated by the movement of the pointer.

Whipple has designed a **fixed focus pyrometer** which consists of a closed tube of fire clay. This is inserted into the furnace or molten metal, the

* Further details are given in *Dict. App. Phys.*, Vol. I, pp. 663-677, in the article on " Total Radiation Pyrometry " by E. Griffiths. Reference may also be made to *Methods of Measuring Temperature* (Griffin, 1925), a book by the same author.

temperature of which is to be found, and the radiation from the hot end is then focused on a minute thermocouple.

In the Foster instrument, the receiving disk on the thermocouple and the front diaphragm of the pyrometer are located at the conjugate foci of the mirror. In the Thawing type the concave mirror is replaced by a cone. The disadvantage of these last two types is that they can only be used with fairly large sources.

Modification for the measurement of very high temperatures, using a rotating sectored disk. If we wish to use a pyrometer to measure temperatures above that for which it is normally calibrated, we can do so by interposing between the hot body and the thermocouple a rotating sectored disk. The object of this disk is to cut down the incident radiation by a definite known fraction. If the sector subtends an angle θ at the centre of the disk, then the fraction of the energy which is transmitted is $\dfrac{2\pi - \theta}{2\pi}$. Let us denote this transmission ratio by R. Let X equal the galvanometer deflection. The pyrometer receives radiation from a black body whose absolute temperature is T_1, when the aperture is clear and the disk is not employed. Let this same deflection X be observed, when the black body is at temperature T_2, and the rotating disk is interposed.

Then, in the first case,　$X = kT_1^4$, where k is some constant,

and, in the second case,　$X = kRT_2^4$.

Thus　　　　　　　　　$T_1^4 = RT_2^4$,

or　　　　　　　　　　$T_2 = \dfrac{T_1}{\sqrt[4]{R}}$.

The above theory has been verified by Mendenhall and Forsythe in the case of two definitely known temperatures, and has been found to hold within the limits of experimental error. The two temperatures taken were the melting point of gold ($1336°$ K.) and the melting point of palladium ($1822°$ K.). The aperture in the sector was cut in the ratio $\left(\dfrac{1336}{1822}\right)^4$ and the deflection was found to be the same at the melting point of gold without the use of the disk, and at the melting point of the palladium when the disk was employed.

2. Optical Pyrometers

Optical pyrometers are simple in construction, and depend upon the comparison between the intensity of radiation of a certain colour emitted by a hot body with the intensity of radiation of the same colour emitted from another body which is at a known temperature.

Total radiation pyrometers are concerned with the full radiation emitted from a black body, that is to say, they take into account radiation

of all wave-lengths. **Optical pyrometers,** or **spectral pyrometers** as they are sometimes called, deal with radiation of one wave-length only, and the intensity of the radiation emitted from a black body in a small width of the spectrum lying between λ and $\lambda + d\lambda$ is compared with the intensity of emission of the same colour from a standard lamp.

Wien's distribution law, $E_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$ is used in order to obtain the relationship between the energy of emission E and the absolute temperature T for any given wave-length λ, c_1 and c_2 being empirical constants. The derivation of this law, and a description of its experimental verification will be given in the following chapter (p. 746). For the present it must suffice to regard the law as being a true representation of the facts.

We will confine ourselves to monochromatic radiation of wave-length λ.

Let E_1 = intensity of emission from the black body at a temperature T_1, and let E_2 = intensity of emission from the standard lamp at a temperature T_2.

Then
$$E_1 = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T_1}},$$

and
$$E_2 = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T_2}},$$

It follows that
$$\log \left(\frac{E_1}{E_2} \right) = \frac{c_2}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

We shall use this equation below, when we are considering the theory of the Wanner pyrometer.

The two best known methods of comparing the intensities of two sources of light may be described as follows :

1. The intensity of the standard light is varied by a known amount until it is equal to the intensity of the source. Pyrometers based on this method are said to be of the **disappearing filament type.**

2. The standard light is kept constant, and the light from the source is varied by means of a polarising device within the instrument itself. Such pyrometers are said to be of the **polarising type.**

1. **Disappearing filament type.** This type of pyrometer was originally devised by Morse in America, about the year 1900. It has more recently been modified and improved by Holborn and Kurlbaum, and by Mendenhall and Forsythe. A modern form of the apparatus is represented diagrammatically in Fig. 270. In this instrument we match the brightness of an electric lamp filament (F) against that of the hot body (H) whose temperature we desire to know. The temperature of the filament is calculated from the knowledge of the current which passes through it

from the battery B. This current is measured by an ammeter A. A rheostat R is also included in the heating circuit, and consequently the temperature and corresponding brightness of the filament can be varied at will. The apparatus is so arranged that the light from the hot body is focused on the filament by means of the lens L. This is then viewed by means of an eyepiece E, which is focused so that both filament and furnace appear in the same plane. If the current through the filament is too strong, the filament will appear bright against the background of the light from the furnace; if the current is too weak it will appear dark. The rheostat is adjusted until the filament disappears. In this case the temperature of the filament will be equal to that of the furnace, which can thus be calculated. It is customary to observe both furnace and the filament through a piece of red glass R, which is inserted
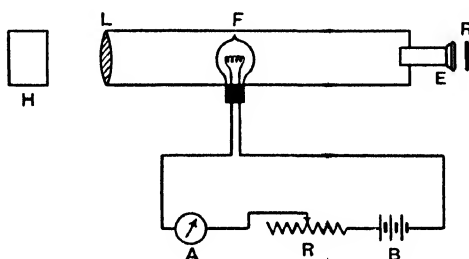
FIG. 270. DISAPPEARING FILAMENT PYROMETER

in the eyepiece. This is done in order that monochromatic radiation may be obtained, and so that colour differences at high temperatures will not render the matching of the intensities more difficult.

The relationship between the current (I) and the absolute temperature (T) may be expressed by the formula $I = a + bT + cT^2$ to a sufficient degree of accuracy. The constants a, b and c may be determined for any given instrument by calibrating it against known temperatures, such as the melting points of different metals. The normal range of temperature which can be measured with this type of instrument is from 600° C. to 1500° C. Above 1600° C., the comparison lamp cannot be used without rapid deterioration. The pyrometer can be adapted for use as high as 2700° C. if a rotating sector is employed to cut out a known fraction of the radiation, as described in the section on radiation pyrometry. The disappearing filament pyrometer is essentially a telescope, and the object whose temperature is desired can easily be selected out of others in the surroundings. Nowadays such instruments are always employed in work of the highest precision, as their simplicity renders possible a high degree of accuracy in their mechanical construction.

2. **Polarising type.** This instrument was first constructed by Wanner in 1901, and is shown in Fig. 271. Light from the two sources which
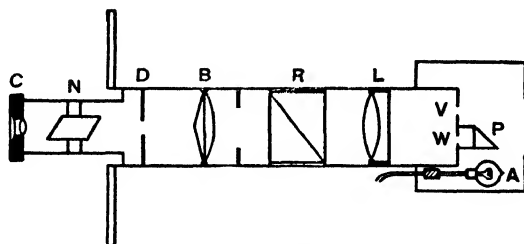
FIG. 271. WANNER'S POLARISING PYROMETER

are to be compared enters the instrument through the two slits V and W. The light from the furnace passes directly through V; the light from the standard lamp A illuminates the matt surface of the right angled prism P, where it suffers total internal reflection and then passes through W. The two beams are each made parallel by means of an achromatic lens L; they then pass through the Rochon prism R, and each beam is thus split up into components polarised at right angles. B is a biprism placed in contact with a second achromatic lens which focuses the two beams on the slit D. The biprism is used in order to produce deviation in the beams of such an amount that an image from each of the two sources is brought into juxtaposition. Since the biprism splits each image up into two, the total number of images has now reached eight. The two images in juxtaposition are polarised at right angles, and appear through the eyepiece C as semicircular patches uniformly illuminated. The remaining six are not needed and are screened out. The Nicol prism N is attached to the eyepiece in such a way that it can be rotated about the optical axis, and its position can be observed by means of an attached pointer.

If the two beams are of equal intensity, and if the plane of polarisation of the Nicol prism makes an angle of 45° with the direction of polarisation of either beam, then in looking through the eyepiece the field would appear to be uniformly illuminated, with a diametrical line across the place where the two fields come in contact. If N is now rotated in either direction the illumination will no longer remain uniform; the intensity of one of the beams will be increased and that of the other decreased. If, however, the beams are originally of unequal intensity, it will be possible to find one position of the Nicol prism between 0° and 90° where the field will appear uniform when viewed through the eyepiece.

The theory of this instrument is as follows :

Let E_1 and E_2 be the intensities of two plane polarised beams of radiation matching a beam of constant intensity, such as that from an

electric lamp, at angles ϕ_1 and ϕ_2, when observed through a Nicol prism. Then, as may be shown by reference to any standard text-book on Optics,

$$\frac{E_1}{E_2} = \frac{\tan^2 \phi_1}{\tan^2 \phi_2}.$$

If we insert a direct vision prism, or a piece of suitable red glass in the apparatus, we can confine ourselves to monochromatic radiation, and can apply Wien's distribution law (page 736).

In this case, $\quad \log\left(\frac{E_1}{E_2}\right) = \frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \log\left(\frac{\tan^2\phi_1}{\tan^2\phi_2}\right).$

Thus we may write

$$2\,(\log \tan \phi_1 - \log \tan \phi_2) = \frac{c_2}{\lambda}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

which gives us a relation between ϕ and T of the form

$$\log \tan \phi = a + \frac{b}{T}, \quad \text{where } a \text{ and } b \text{ are constants.}$$

These constants can be determined for any given instrument by calibrating it against a black body radiator at various known temperatures which are measured by means of a standardised thermocouple.

The polarising pyrometer has a normal range of temperature from 700° to 1400° C. Below 700° C., the light transmitted is too feeble to make accurate observations. The instrument is essentially a photometer, and it is legitimate to extrapolate the scale on the basis of Wien's law. It is possible to extend the readings of the apparatus by inserting absorption glasses of appropriate density between the source and the pyrometer. With one glass interposed, the scale will read from 900° to 2000° C., with two glasses, from 1200° to 2500° C., and with three glasses, from 1400° to 4000° C. This is sufficient for all eventualities, because 4000° —the temperature of the electric arc—is the highest known terrestrial temperature.

To ensure that the temperature scale may be independent of any variation in the comparison electric lamp, this lamp must be checked from time to time against a standard amyl acetate lamp.

QUESTIONS

CHAPTER XXXVII

1. Discuss methods of detecting radiant heat. (E.U., Inter. Hons.)

2. Describe a sensitive and accurate instrument for measuring very small quantities of thermal radiation.
What is meant by the " full radiation " corresponding to a particular temperature, and how can it be realised experimentally ?

3. Describe how the platinum resistance thermometer and the thermo-electric thermometer have been modified to provide means for the accurate measurement of thermal radiation.

4. State Stefan's law of radiation, and explain how it may be experimentally verified.

Calculate the maximum net rate of loss of heat by radiation from a sphere of 10 cm. radius at a temperature of 200° C. when the surroundings are at a temperature of 20° C., if Stefan's constant is $5 \cdot 7 \times 10^{-5}$ erg cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$.

(L.U., B.Sc.)

5. Give a physical explanation of the pressure exerted by radiation on matter on which it is incident, and describe in detail the experiment of Nichols and Hull on the measurement of this pressure.

It is estimated that, were it not for absorption in the atmosphere, the radiation received from the sun would amount to about 2 calories per sq. cm. per minute. Calculate the pressure this radiation would exert on a perfectly absorbing surface on which it fell normally.

(E.U., M.A. Hons.)

6. Describe in detail an optical pyrometer or any other arrangement which may be used for the measurement of very high temperatures.

(St. A. U.)

7. What is meant by the phrase *total radiation* ?   Mention the two chief types of total radiation pyrometers, and describe in detail *one* such instrument.

8. Explain how the colour of radiation may be used to determine the temperature of the source.   Describe one form of Optical Pyrometer.

9. Describe the principles and methods of the measurement of temperatures in the neighbourhood of 2000° C.

(L.U., Spec. B.Sc.)

10. Prove Larmor's theorem which states that the normal pressure of diffuse radiation falling in all directions on a surface is equal to one-third of the energy density.

CHAPTER XXXVIII

THE LAWS OF RADIATION

In Chapters XVIII and XX we considered the radiation of heat from an elementary standpoint, and in Chapter XXXVII we described various methods of measuring high temperatures, using total radiation or optical pyrometers. Now we must discuss the fundamental laws of radiation upon which such measurements depend. First of all, we shall derive these laws theoretically from a consideration of thermodynamics, and afterwards proceed to a description of their experimental verification. The three principal laws are **Stefan's Fourth Power Law**, and two other laws derived from it by Wien, known as **Wien's Displacement Law**, and **Wien's Distribution Law**, respectively.

SUMMARY OF THE RADIATION LAWS

Stefan's law was first derived empirically from some observations on Tyndall's experiments on the radiation from platinum wire when heated to different known temperatures. Afterwards in 1884, Boltzmann deduced it theoretically from the principles of thermodynamics; it is sometimes known as the Stefan-Boltzmann law.

The law states that the energy E_r of all wave-lengths passing *in unit time* in the form of radiation from a uniformly heated enclosure at absolute temperature T_1 to another body at absolute temperature T_0 is proportional to the fourth powers of their absolute temperatures, or

$$E_r = \sigma(T_1{}^4 - T_0{}^4),$$

where σ is a constant, known as **Stefan's Constant**. Note that E_r is the *rate* of transfer of energy per unit area.

Stefan's law has been verified experimentally by Lummer and Pringsheim for black body radiation. Methods for determining the value of σ are given below (p. 750).

Wien's displacement law was put forward in 1896, and may conveniently be written in either of the forms

$$\lambda_m T = \text{const.} = A \text{ (say)},$$

or
$$E_m T^{-5} = \text{const.} = B \text{ (say)},$$

where λ_m is the wave-length for which the energy is a maximum, E_m the maximum value of the energy density, and T the absolute temperature.

Wien's distribution law shows the distribution of the energy among the different wave-lengths of the spectrum, and may be written

$$E_\lambda = C\lambda^{-5}f(\lambda T),$$

where E_λ is energy emitted in the range of wave-lengths between λ and $\lambda + d\lambda$, C is a constant, and $f(\lambda T)$ is a function which cannot be further determined by purely thermodynamical reasoning. Various attempts to evaluate this unknown function have been made; these will be considered later.

We shall now give the theoretical proofs of these three laws.

THEORETICAL DISCUSSION

Stefan's law. The proof given below, which is due to Boltzmann, depends upon a knowledge of Maxwell's electromagnetic theory of light. According to this theory when light falls perpendicularly upon a perfectly reflecting plane surface, it exerts a pressure p on the surface equal to the energy density E of the radiation. If, however, instead of a parallel beam, the light is diffuse and is incident in all directions, then the pressure is equal to one-third of the density of the energy, and $p = \frac{1}{3}E$. This is analogous to the pressure of a gas, and has already been discussed on p. 728. If, then, a reflecting surface be moved against incident radiation, work must be done.

Let us consider a cylinder $ABCD$ of unit cross-section with perfectly reflecting walls, and provided with a perfectly reflecting piston P. We assume that the sides of the enclosure are also perfectly reflecting, so that no heat transference will take place between the radiation and the walls. We can consequently ignore the thermal capacity of the latter. We assume that the enclosure is filled with radiation at a uniform temperature T, due to an infinitesimal amount of matter whose heat energy may be neglected.

Now let us suppose that a small quantity of heat dQ flows into the enclosure from outside, and at the same time the volume is allowed to change from v to $v + dv$. The temperature T, and consequently the energy density E, also changes by an infinitesimal amount. The change is assumed to be reversible, but is neither isothermal nor adiabatic.

The thermodynamic equation of work becomes

$$dQ = dU + dA,$$

where U and A are the internal energy, and external work respectively.

Since E is the energy density, or energy of radiation per unit volume, we have $U = Ev$.

Let p be the pressure (force per unit area) exerted on the piston by the radiation inside the enclosure. Then $dA = p\, dr$.

Now we have already seen that for diffuse radiation the pressure per unit area is equal to one-third of the energy per unit volume, so we may write $p = \frac{1}{3}E$.

Therefore the equation $\qquad dQ = dU + dA$

becomes $\qquad dQ = d(Ev) + \frac{1}{3}E\, dv = v\, dE + \frac{4}{3}E\, dv.$

If S is the entropy of the radiation, then

$$dS = \frac{dQ}{T} = \frac{v}{T}\, dE + \frac{4}{3}\frac{E}{T}\, dv.$$

Now dS must be a perfect differential,

$$\therefore\ dS = \frac{\partial S}{\partial E}\, dE + \frac{\partial S}{\partial v}\, dv.$$

Therefore, comparing the two last equations, we have

$$\frac{\partial S}{\partial E} = \frac{v}{T}, \quad \text{and} \quad \frac{\partial S}{\partial v} = \frac{4}{3}\frac{E}{T}.$$

Applying the condition for a perfect differential (p. 649) we find

$$\frac{\partial}{\partial v}\left(\frac{v}{T}\right) = \frac{4}{3}\frac{\partial}{\partial E}\left(\frac{E}{T}\right).$$

Now T is independent of v, and is a function of E only,

$$\therefore\ \frac{1}{T} = \frac{4}{3}\cdot\frac{1}{T^2}\left(T - E\frac{\partial T}{\partial E}\right);$$

$$\therefore\ 1 = \frac{4}{3}\left(1 - \frac{E}{T}\frac{\partial T}{\partial E}\right.$$

$$\therefore\ \frac{4}{3}\frac{E}{T}\frac{\partial T}{\partial E} = \frac{1}{3};$$

$$\therefore\ 4\frac{\partial T}{T} = \frac{\partial E}{E}.$$

On integration, $\qquad \log E = 4\log T + \text{const.}\,;$

$$\therefore\ E = aT^4,$$

where a is a constant called the total radiation density constant.

As we have already seen, this law is only strictly valid for the transference of heat between " black " bodies, and we may enunciate the formal definition of the Stefan-Boltzmann law as follows :

If a black body at absolute temperature T_1 be surrounded by another black body at absolute temperature T_0, the amount of energy E_r lost per second per unit area of the former is

$$E_r = \sigma(T_1^4 - T_0^4).$$

Wien's displacement law. Now let us consider an adiabatic expansion; as in the previous case, the thermodynamic equation for any expansion is

$$dQ = d(Ev) + \tfrac{1}{3}E \, dv.$$

If the expansion is *adiabatic*, then $dQ = 0$, and

$$\tfrac{4}{3}E \, dv + v \, dE = 0 \; ;$$

$$\therefore \; \frac{4}{3}\frac{dv}{v} + \frac{dE}{E} = 0.$$

On integration,

$$\tfrac{4}{3} \log v + \log E = \text{const.} \; ;$$

$$\therefore \; v^{\frac{4}{3}} E = \text{const.} = v^{\frac{4}{3}} T^4 \sigma \; ;$$

$$\therefore \; v^{\frac{1}{3}} T = \text{const.}$$

We must now find the change in wave-length suffered by a ray reflected at a surface moving with a velocity u.

Consider the state of affairs indicated in Fig. 272 (*a*).
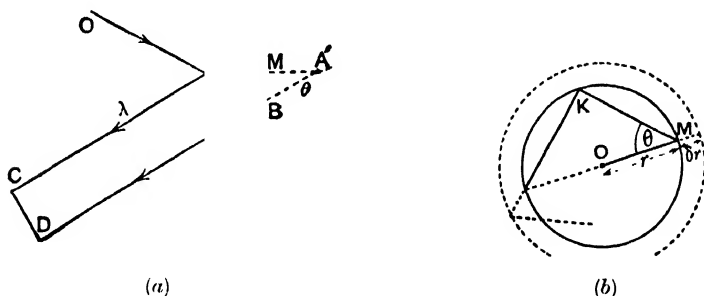
FIG. 272. DERIVATION OF WIEN'S DISPLACEMENT LAW

Let OA be the incident ray falling on the mirror AX, and let θ be the angle of incidence. A particular wave-crest strikes the mirror at A and is reflected to C. Let $AC = \lambda$, the wave-length, so that the first wave-crest has reached C when the next is at A. In the meantime the mirror has moved a distance AM or $u\tau$, where τ is the period of the wave-motion. The path followed by the second wave-crest is ABD, which is equal to $A'D$ or $A'N + ND$. Hence the increase of wave-length $\delta\lambda$ is $A'N$, so that we get

$$\delta\lambda = AA' \cos\theta = 2u\tau \cos\theta.$$

Now the time τ is (to the first order) $= \lambda/c$, where c is the velocity of light.[*]

$$\delta\lambda = \frac{2\lambda u \cos\theta}{}$$

* This assumes that the time taken by the wave to travel over AC and the mirror to recede from A to M is the same, neglecting the time taken by the second wave to traverse AB, which is a very small time-interval.

This is the change of wave-length due to *one* reflection at the moving surface.

Consider a sphere of radius r_0 expanding uniformly with a velocity u (Fig. 272 (b)).

Then, at any time t, we have $r = r_0 + ut$;

$$\therefore \; \delta r = u \delta t.$$

If a ray (not shown in the diagram) strikes the surface of the sphere and is reflected in the direction MK, making an angle θ with the normal, then the distance it travels before suffering another reflection is

$$MK = 2r \cos \theta.$$

The time between each successive reflection $= \dfrac{MK}{c} = \dfrac{2r \cos \theta}{c}$.

Hence the number of reflections in time δt, that is, while the radius increases by δr

$$= \frac{c}{2r \cos \theta} \delta t = \frac{c}{2u \cos \theta} \times \frac{\delta r}{r}.$$

The change of wave-length in time δt, and corresponding to δr, is

$$\delta \lambda = \frac{2\lambda u \cos \theta}{c} \times \frac{c}{2u \cos \theta} \times \frac{\delta r}{r}$$

$$\therefore \; \frac{\delta \lambda}{\lambda} = \frac{\delta r}{r} = \frac{1}{3} \frac{\delta v}{v}, \text{ where } \delta v \text{ is the change in volume } v.$$

On integration, $\log \lambda = \frac{1}{3} \log v$; or $\lambda = v^{\frac{1}{3}}$;

and, combining this with the above equation $v^{\frac{1}{3}} T = \text{const.}$, we obtain the relation $\lambda T = \text{const.}$

This equation, which is the usual statement of Wien's displacement law, expresses the fact that if radiation of a particular wave-length whose intensity corresponds to a particular temperature is adiabatically altered to another wave-length, then the temperature changes in the inverse ratio.

Wien's distribution law. From the two last theorems we can now establish a relation for the distribution of energy in the spectrum.

Consider the energy in a small strip, between the wave-lengths λ and $\lambda + d\lambda$ (Fig. 273).

It is obvious that the energy of the strip, $E_\lambda d\lambda$, must be some function of the temperature T, and also of the constant λT. Also the function of T must be proportional to T^4.

Hence we may write $E_\lambda d\lambda = aT^4 f(\lambda T) d(\lambda T)$. [$a$ is a constant.]
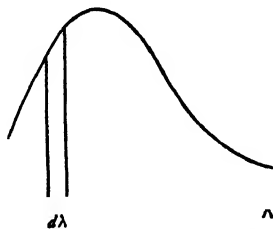
FIG. 273. DERIVATION OF WIEN'S DISTRIBUTION LAW

Now, since we may regard the temperature as constant for the small strip, we may write the last differential in the form $T \, d\lambda$.

$$\therefore \; E_\lambda \, d\lambda = bT^5 f(\lambda T) \, d\lambda;$$

$$\therefore \; E_\lambda T^{-5} = \text{const.} = bf(\lambda T). \qquad [b \text{ is a constant.}]$$

We have already shown that $\lambda T = \text{const.}$, and consequently we may write

$$E_\lambda = C\lambda^{-5} f(\lambda T). \qquad [C \text{ is a constant.}]$$

This is the most common way of expressing Wien's distribution law.

It is not possible to determine the form of the function $f(\lambda T)$ by purely thermodynamic reasoning, but by making certain arbitrary assumptions concerning the radiation emitted by the gaseous molecules, Wien was able to establish a relationship of the form

$$E_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}},$$

where c_1 and c_2 are constants.

In this equation $E = 0$, for $\lambda = 0$ and $\lambda = \infty$, and we obtain a maximum value for E, agreeing with experimental observations. But, if $T = \infty$, E is still finite, and Lord Rayleigh has pointed out that this is unlikely to be true. Rayleigh's own formula, and that proposed by Planck using the Quantum Theory, are discussed later on p. 762.

EXPERIMENTAL VERIFICATION OF THE LAWS OF RADIATION

Lummer and Pringsheim's experiments on Stefan's law. In 1897, Lummer and Pringsheim undertook some preliminary experiments in order to verify Stefan's law. Their apparatus is illustrated in Fig. 274.
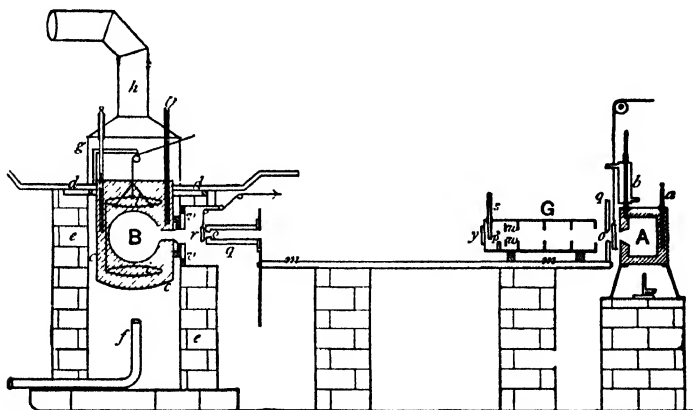
FIG. 274. LUMMER AND PRINGSHEIM'S APPARATUS FOR THE VERIFICATION OF STEFAN'S LAW

A and *B* are vessels coated inside with platinum black, and are heated up to known temperatures to be used as the sources of radiation. *A* is surrounded by a bath of boiling water, and *B* by a bath of nitre which could be kept at a known temperature. Water baths were provided at the opening of *B*, and also at the diaphragm *q*, and movable shutter *r* ; these could be accurately kept at a known temperature corresponding to T_0 in the equation.

In making an observation the shutter *r* was raised, thus allowing the energy to fall on the surface of the Lummer-Kurlbaum bolometer *G*, which was used to measure the radiant energy. The resulting deflection of the galvanometer was observed.

The nitre bath was used with the vessel *B* between 200° and 600° C., but above that temperature an iron cylinder heated by a gas furnace was employed up to 1300° C. The vessel *A* was simply used as a standard of reference in both series of experiments. In order to show that the deflection was proportional to the energy of the incident radiation, readings were taken with the bolometer at different distances from the black body. It was found that the inverse square law was satisfied.

When the temperature of the black body was varied, and measured directly, it was found that Stefan's law held, and that the total radiation was proportional to the fourth power of the absolute temperature.

Lummer and Pringsheim's experiments on Wien's law. Two years later, in 1899, Lummer and Pringsheim modified their apparatus in order to determine the distribution of energy in the spectrum of a " full radiator " or " black body ". At first they employed for the source of radiation the various types of uniformly heated enclosures, already described above, in connection with their experiments on Stefan's law, but later they used an electrically heated carbon tube. This is described fully in the next section, which deals with their final and extremely accurate experiments. The spectrum of the full radiation was produced by refraction through a fluor-spar prism, fluor-spar being very transparent to the infra-red radiations. It was necessary to apply corrections in order to convert the prismatic to the normal energy curves, and for this purpose the known dispersion curve of fluor-spar was employed. The distribution of energy was measured by means of a linear bolometer (see p. 749), which was enclosed in an air-tight case in order to diminish the absorption effects due to water vapour and carbon dioxide. The image of the slit was focused on the bolometer by means of a concave mirror, as a glass lens would have caused absorption effects.

The distribution curves obtained in this way are shown in Fig. 275 for temperatures of the black body ranging from 700° to 1600° C. The ordinates represent emissive powers (E) or intensities of radiation, and the abscissae are wave-lengths (λ) between 6μ and the beginning of the visible spectrum. Strictly speaking the ordinate E_λ is the energy per unit range of wave-length.
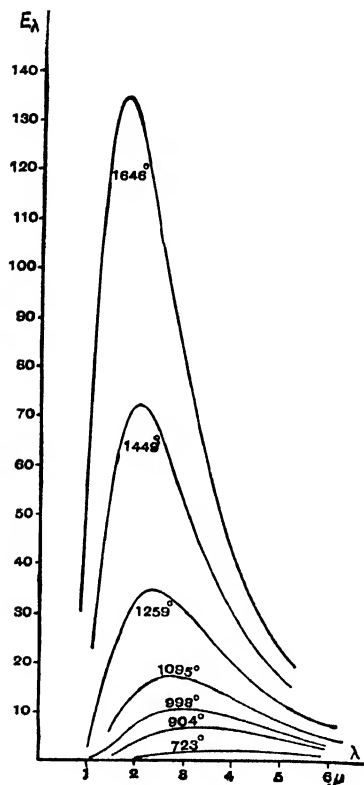
FIG. 275. DISTRIBUTION OF ENERGY IN THE SPECTRUM OF A BLACK BODY

From these curves it is possible to obtain the values of E_m and the corresponding λ_m for any given value of T, and it is found that both the displacement and distribution laws of Wien are valid within the limits of experimental error. Further, the total radiation E at any absolute temperature T is represented by the area enclosed between the corresponding curve and the x-axis. The value of this area is found to vary as T^4, thus demonstrating the truth of Stefan's law.

Lummer and Pringsheim's experiments on the measurement of high temperatures. In 1903, Lummer and Pringsheim made a still more accurate series of experiments in order to show that the radiation laws afford a suitable means for the accurate measurement of high temperatures. They constructed a special radiating chamber in which the conditions of "black body radiation", or "full radiation" were practically fulfilled (see Fig. 276). A carbon tube R, carefully made so as to be exactly cylindrical in form, was heated electrically, and formed the radiating body. The current was conveyed through carbon blocks A at the end of the tube, which was supported in metal clamps B through which the current also flowed. Plugs P_1 and P_2 were inserted symmetrically in the tube in order to exclude any oxygen, and to keep the tube as air-tight as possible. The whole system was surrounded by a series of enclosures, in order to keep the carbon from burning. A continuous stream of nitrogen preserved the tube from being destroyed by oxidation at the open end F.

A special bolometer was designed for these experiments (see p. 724), depending upon the change in electrical resistance of strips of platinum foil, when exposed to radiation. Four zigzag strips were used, and formed the four arms of a Wheatstone bridge. Two gratings belonging to opposite arms of the bridge were placed together, so that the strips of one covered the gaps of the other, thus doubling the effect. It proved to be an additional advantage to have four strips, for any outside temperature change affected them all equally, and consequently there was no change in the zero of the galvanometer.
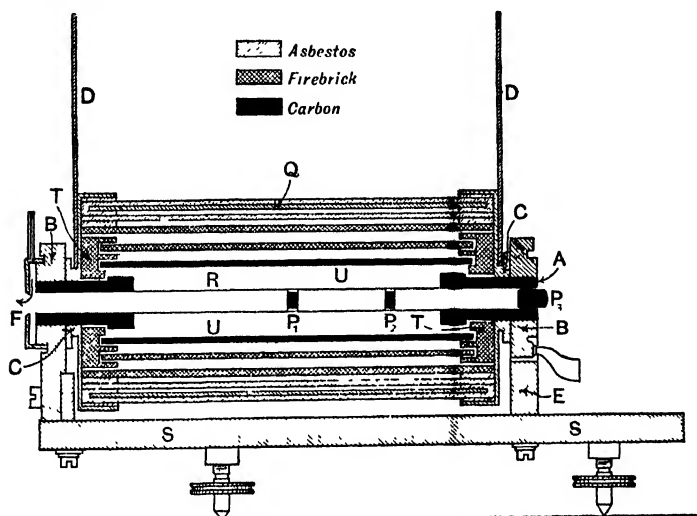
FIG. 276. LUMMER AND PRINGSHEIM'S " BLACK BODY " FOR THE MEASUREMENT OF HIGH TEMPERATURES

For the determination of the energy distribution curves, they used a linear spectrum bolometer, as in their earlier experiments. A single narrow strip of platinum replaced the grating, and thus any required spectral line could be isolated. The refracting prism was again made of fluor-spar.

Lummer and Pringsheim also made some experiments on brightness of different portions of the luminous spectrum, and matched the black body radiation against that of a known temperature, using a specially designed photometer.

From all these experiments it was shown that measurement of temperature by radiation was both practicable and accurate, although it is necessary to calibrate all the instruments against the gas scale, by means of a resistance or a thermoelectric thermometer. In Lummer and Pringsheim's experiments the different instruments were calibrated by an

electrically heated black body, the temperature of which was measured
with a standard thermoelement.   ˈ

ABSOLUTE MEASUREMENT OF RADIATION

The measurement of radiant energy in absolute units is of considerable
importance.   A type of experiment which is the basis of the determin-
ation of several physical constants, consists in comparing the heating
effect of radiation with the same heating effect produced electrically.   Let
us consider radiation from a black body B falling on a receiver R. R may
be any instrument suitable for measuring radiation, for example, a
bolometer or a radiomicrometer.   In many cases it is possible to produce
the same effect in R by heating it with an electric current.   It is possible
to determine the value of the energy associated with the flow of the
current in absolute units.   This value can then be equated to the radiant
energy, the absolute value of which can thus be determined.   The
experimental conditions naturally vary with the actual problem which
is to be solved, but the general method is of wide application.   We
shall proceed to apply it to two important problems, (1) the determin-
ation of the constant of total radiation σ, sometimes called **Stefan's
Constant,** and (2) the determination of the radiation from the sun, or
the **Solar Constant.**

   1. **Stefan's constant.**   We have already seen that the formal statement
of the Stefan-Boltzmann law is

$$E_r = \sigma(T_1{}^4 - T_0{}^4),$$

where E_r is the radiant energy emitted from the surface of a black body
per sq. cm. per sec. ;

   T_1 is the absolute temperature of the surface ;

   T_0 is the absolute temperature of the surroundings receiving the
      radiation.

This equation defines σ, Stefan's constant, and we can see at once that,
in absolute units, it will be expressed in erg cm.$^{-2}$ sec.$^{-1}$ °C.$^{-4}$.

Many workers have undertaken experiments with a view to determining
the value of σ.   In 1916, Coblentz measured the energy of radiation
coming from a black body consisting of a diaphragmed porcelain tube,
wound with platinum and heated electrically.   The method of observa-
tion consisted in exposing the receiver to the radiation, and noting the
deflection in a sensitive galvanometer in a thermoelectric circuit, the hot
junction of which was on the back of the receiver, and at the same
temperature.   The strip was then heated electrically to give the same
deflection, and the electrical energy put in could be calculated from the
values of the current and resistance.   Hence the energy of radiation

falling on the receiver was known and thus σ could be calculated directly from Stefan's law. The range of temperature that Coblentz used was $800°$-$1100°$ C., and the mean value for σ after correction for loss of energy due to reflection, and other errors, was found to be

$$\sigma = 5\cdot72 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ °C.}^{-4}.$$

Müller, in 1923, used a somewhat similar method, and employed a large square plate as a receiver. This in turn radiated to a surface bolometer ; the uncertainty in the effective size of the plate was thus reduced to a minimum. The value obtained was

$$\sigma = 5\cdot77 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec. }^{-1} \text{ °C.}^{-4}.$$

A critical discussion on the results obtained by various workers, and the different methods employed, has been given by Birge.* He finally adopted a most probable value of

$$\sigma = 5\cdot735 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ °C.}^{-4}.$$

2. **The solar constant.** The sun emits radiant energy in all directions by virtue of its temperature. Only a small fraction of this radiation reaches the earth, but this fraction is sufficient to provide the heat and light necessary to maintain human, animal, and vegetable life. The amount of radiation actually received at any one place and time depends upon many variable factors, such as the season of the year, the time of day, and the amount of absorption due to the earth's atmosphere. Consequently in order to obtain a constant value, we must postulate ideal conditions. The **solar constant** is therefore defined as the amount of energy which is absorbed per minute by one square centimetre of a perfectly black surface held at right angles to the sun's rays, and placed at the mean distance of the earth from the sun in the absence of the atmosphere.

Pyroheliometers. Instruments which are used for the measurement of the solar constant are known as **pyroheliometers.** One of the best known is the Ångström pyroheliometer, which employs the method already described of equality of heating due to radiation and due to the passage of an electric current The principle is simple, and the essential apparatus consists of two thin metal strips, usually made of manganin. These are alternately exposed to radiation from the sun. When one strip is being heated, the other one is shielded from the radiation, and then heated to the same temperature by means of an electric current. A pair of copper-constantin thermojunctions are attached to the back of the receiving strips, but are insulated from them ; equality of temperature is shown by a sensitive galvanometer which is included in the circuit.

* Birge, *Reviews of Modern Physics*, Vol. 2, p. 56 (1930).

Another type of apparatus in use at the Smithsonian Institution in Washington is known as the Water-Stir Pyroheliometer. It is illustrated in Fig. 277. The radiation is received in the black body chamber AA
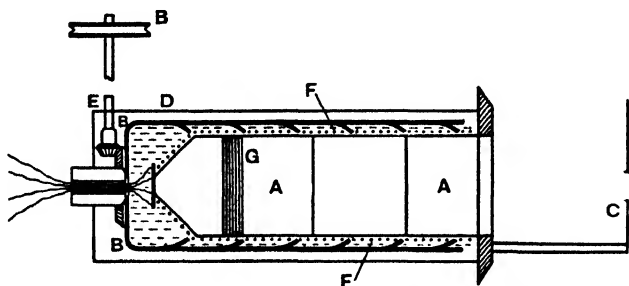
FIG. 277. WATER-STIR PYROHELIOMETER

which has its rear end of conical shape. This chamber is blackened inside and is surrounded by a calorimeter DD containing water which is stirred vigorously by the apparatus BB driven by an electric motor. C is a diaphragm of known aperture through which the solar radiation is admitted. The energy of the radiation is completely absorbed in the chamber, and the resulting rise in temperature of the water is measured by means of the platinum resistance thermometer FF whose wire is wound on an insulating frame round AA. Near E is inserted a mercury thermometer. In order to calibrate the apparatus, another experiment is made. A known electric current is sent through a manganin resistance wire under similar conditions, and the rise in temperature of the water is again observed. Thus the heat generated electrically can be compared with that received from the solar radiation.

A similar type of instrument is known as Abbott and Fowle's Water-Flow Pyroheliometer. In this case a steady stream of water flows past the absorption chamber, and the difference in temperature between the incoming and outgoing water is measured.

The **mean value** for the solar constant has been found to be 1·937 calories per sq. cm. per minute, but it is very probable that this quantity is not, in reality, constant, and varies with astronomical conditions.

The temperature of the sun. Closely allied to the determination of the solar constant is the problem of finding the temperature of the sun. The mathematical calculation of this lies outside the scope of this work, but the temperature is now generally assumed to be in the neighbourhood of 6000° K.

QUESTIONS

Chapter XXXVIII

1. Explain what is meant by " black body radiation ". Give a brief account of its laws, explaining how they have been investigated.   (E.U., Inter. Hons.)

2. Describe how the wave-lengths of the radiations sent out by a heated body may be determined. Show by curves how their intensity may vary with the temperature of the body.   (L.U., B.Sc.)

3. What is meant by a *black body radiator*? How can it be realised **experi**mentally ?
Sketch and describe the energy distribution curves of radiation from a black body at different temperatures, and show how from measurements of the spectral energy curve of solar radiation the sun's temperature may be estimated.
            (L.U., B.Sc.)

4. Given the distribution of energy in the spectrum of the radiation from a full radiator, show how it may be found at any other temperature.
Give the theoretical derivation of the laws upon which the method is based.
            (Camb. Part II Tripos.)

5. Derive the relationships upon which practical radiation methods of determining high temperatures are based, and indicate how the methods are applied in practice.   (Camb. Part II Tripos)

6. What do you understand by the term " black body " ?
Discuss the relation between the total radiation from such a body and its absolute temperature
Compare the rates of loss of heat from a body at 1000° C. and from the same body at 500° C., assuming that it is placed in an enclosure at 15° C.

7. What is meant by " full " or " black body " radiation ? Write an account of experiments to determine the distribution of energy in the spectrum of such radiation, and mention some of the results obtained.

8. Prove that diffuse radiation exerts, at any place on the walls of a cavity in which it is confined, a pressure equal to one-third of its energy density.
Assuming that when the cavity changes its volume, while retaining its shape, the wave-lengths change in the same ratio as the linear dimensions of the cavity, show that when diffuse radiation of wave-lengths between λ and $\lambda + d\lambda$ and of energy density $E_\lambda d\lambda$ is compressed adiabatically, E_λ varies as λ^{-5}.
Hence, assuming the displacement law, $\lambda T =$ constant, deduce the formula for the distribution of energy in the spectrum

$$E_\lambda = \frac{1}{\lambda^5} f(\lambda T).$$

State the nature of the argument which led to the introduction of the quantum theory as an explanation of observed facts of radiation.   (E.U , M.A. Hons.)

9. Describe an accurate method which has been used for the determination of Stefan's Constant.

10. What is meant by the expression *a pyroheliometer*? Describe one such instrument and explain how it has been used to determine the value of the Solar **Constant.**

THE QUANTUM THEORY OF RADIATION

THE RADIATION PROBLEM AND PLANCK'S SOLUTION

The distribution of energy in the spectrum. The quantum theory originated in an attempt to account for a startling discrepancy between theory and experiment as to the way in which energy is distributed in the spectrum of a full radiator or perfectly black body. We may recall the result implicit in Prévost's theory of exchanges that all bodies are continually radiating heat, so that a body at an assigned temperature is giving out energy in the form of radiation of all wave-lengths or all possible frequencies of vibration. To any particular wave-length, λ, there corresponds a definite frequency of vibration, ν, in accordance with the relation

$$c = \nu\lambda,$$

where c is the velocity of light. In theoretical work it is often preferable to specify the colour of a ray of light by its frequency rather than its wave-length, since the latter depends upon the medium through which the light is passing. A very small spectral region with frequency lying between the limits ν and $\nu + d\nu$ corresponds to what would be described in experimental work as monochromatic radiation. In terms of the wave-length, the *interval* corresponding to $d\nu$ is given by

$$d\lambda = -\frac{c}{\nu^2}\,d\nu,$$

the negative sign arising from the fact that as ν increases λ diminishes.

It is to be noted that we are now concerned only with " temperature radiation ", in which the supply of radiant energy is derived from the heat energy of the hot body, and not with " luminescence ", in which the energy of radiation is derived from some other source, for example chemical action. The laws which govern radiation due to temperature alone have been discussed in the previous chapter, but for completeness they will be summarised briefly here.

According to Balfour Stewart and Kirchhoff there is a simple relation between the emissive power of any body at a particular temperature and its absorptive power. For our present purpose the emissive power E

may be defined as the intensity of radiation of given wave-length emitted at the assigned temperature, and the absorptive power A as the fraction of incident radiation absorbed by the body. Then the ratio of the emissive power to the absorptive power E/A is a function only of the temperature and the wave-length of the radiation concerned. A body for which $A = 1$ is said to be perfectly absorbing or " perfectly black ". The exact implications of this term have been discussed by Kirchhoff ; * it need only be pointed out that strictly speaking the definition refers to rays of one definite colour only. If the emissivity of a " black " body be denoted by E_b, we have the general relation

$$\frac{E}{A} = E_b.$$

Let us now consider a number of bodies of various materials enclosed in a chamber having walls which are impermeable to heat. Then, no matter what may be the initial temperatures of the bodies, in course of time a steady state will be reached in which all the bodies will be at the same temperature. This is the state of **thermodynamic equilibrium** in which, in accordance with the second law of thermodynamics, the entropy of the system has a maximum value. The radiation which now traverses all parts of this uniform temperature enclosure may be termed **equilibrium radiation**. Since one of the bodies may be regarded as " black " for all kinds of radiation, this equilibrium radiation is sometimes called **black radiation**.

Suppose a hollow chamber, having a small hole in its side, is maintained at a uniform temperature. Then it is found that the spectrum of the radiation issuing from the hole is independent of the material of the walls and depends only on their temperature.

The radiation coming out of the chamber may be called the **complete** or **full radiation** corresponding to that temperature. *If it be assumed* that a state of thermodynamic equilibrium has been reached inside the chamber, the " full " radiation may be regarded as at any rate a close approximation to " equilibrium " radiation. This method of experimenting with " black body " radiation is due to Lummer and Wien.†

The next step is to determine the state of the field inside the uniform temperature enclosure. It may be shown‡ that the radiation field is a truly isotropic one, the propagation taking place in the same manner in all directions, and that the amount of energy present in unit volume, so far as it is due to rays having wave-lengths between the limits λ and $\lambda + d\lambda$, is

$$\frac{8\pi}{c} E_b \, d\lambda.$$

* See Planck's *Heat Radiation*, § 10 (1914).

† Lummer and Wien, *Wied. Ann.*, Vol. 56, p. 451 (1895)

‡ See Lorentz, *The Theory of Electrons*, § 52.

This **energy density** may also be written in the form

$$E_\lambda d\lambda = F(\lambda, T) d\lambda,$$

where F is a function of the two variables λ and T, and T is the absolute temperature of the radiator.

Thus by employing the previous relation we may put

$$E_\lambda = F(\lambda, T) = \frac{8\pi}{c} E_b = \frac{8\pi}{c} \frac{E}{A}.$$

The problem to be solved is the determination of the form of this function F, which determines the distribution of energy in the spectrum of a full radiator at any assigned temperature.

The results of experiment. The experimental results obtained by Lummer and Pringsheim, and confirmed by other investigators, may be taken by way of illustration. The spectrum of the full radiation was produced by refraction through a prism of fluor-spar, a concave mirror being employed to obtain an image of the slit. This image was focused on a linear bolometer, which was used to measure the radiant energy. The results can best be understood by reference to Fig. 275, where the energy is plotted against the wave-length. For a particular temperature of the radiator, the curve obtained shows a maximum for some wave-length in the infra-red, the general shape of the curve being similar to that which represents the distribution of velocities amongst the molecules of a gas in Maxwell's theory. The energy radiated is found to be extremely small both for very long and for very short waves. As the temperature of the radiator is increased, the *total* amount of energy radiated increases in proportion to the fourth power of the absolute temperature, in accordance with Stefan's law, which may be written

$$\int_0^\infty E_\lambda d\lambda = a T^4,$$

where a is constant.

The theoretical proof of Stefan's empirical law due to Boltzmann, who based his work on thermodynamic and electrodynamic principles, has already been given on p. 742. Coblentz * and Millikan by independent methods find

$$a = 7 \cdot 63 \times 10^{-15} \text{ erg. cm.}^{-3} \text{ degree}^{-4}.$$

The corresponding value of Stefan's radiation constant σ, which represents the total energy radiated (of all wave-lengths) from unit area of a full radiator in unit time, is

$$\sigma = \frac{ac}{4} = 5 \cdot 72 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg. C.}^{-4}.$$

Birge (1930) gives a value $\sigma = 5 \cdot 735 \times 10^{-5}$ erg cm.$^{-2}$ sec.$^{-1}$ deg. C.$^{-4}$.

Accompanying this increase in the total radiant energy there is a shift in the position of the maximum, which is now more sharply defined,

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* Coblentz, *Bureau of Standards, Scientific Papers*, Nos. 357, 360 (1920.)

towards the region of short wave-lengths. If λ_m denote the value of the wave-length corresponding to the energy maximum, Wien's law states that

$$\lambda_m \times T = \text{a constant} = b \text{ (say)}.$$

The experiments of Lummer and Pringsheim gave as the value of this constant 0·2940 cm. deg. Later experiments by Coblentz give $b = 0·2885$ cm. deg.

The results of the classical theory. These experimental results are in conflict with the theoretical relation deduced by the application of the principle of the equipartition of energy, which is based upon the classical dynamical laws. Lord Rayleigh showed that this relation, which will be discussed more fully later, requires that the energy distribution should be given by

$$E_\lambda d\lambda = 8\pi kT\lambda^{-4} d\lambda$$

where k is Boltzmann's constant. This formula shows no trace of a maximum in the curve connecting energy and wave-length, on the contrary the energy should increase without limit as the wave-length is diminished, and the total energy for all wave-lengths is necessarily infinite.

It has been clearly pointed out by Jeans in his valuable *Report on Radiation and the Quantum Theory** that the crucial test of the Newtonian mechanics is the phenomenon that **the total radiant energy per unit volume of ether in temperature-equilibrium with matter is finite, and not infinite.** Jeans illustrates this by considering a mass of iron coated with a perfectly absorbing paint, placed in a uniform temperature enclosure at 0° C. Each square centimetre of surface emits 3×10^5 ergs of radiation per second into the ether, and also absorbs 3×10^5 ergs per second of radiation falling on to it from the ether. The energy in the ether is of density 4×10^{-5} ergs per cubic centimetre ; the heat energy in the iron is of the order of 8×10^9 ergs. per c.c., or about 2×10^{14} times as great.

Analogies given by Jeans. " A very little consideration will show that this state of things is different from what might be expected by analogy from other systems which are known to obey the ordinary dynamical laws. Consider, for instance, a tank of water (to represent the ether) in which is floated a system of corks (to represent atoms of matter) connected by light springs or elastics so that they can oscillate relatively to one another. Suppose that initially the surface of the water is at rest. Let the system of corks be set into violent oscillation and placed on the surface of the water. The motion of the corks will set up waves in the water, and these waves will spread all over the surface of the water, undergoing reflection when they meet the walls of the tank. We know that ultimately the corks will be reduced to rest ; the energy of their motion will be transformed first into the energy of waves and ripples on

* *Report of the Physical Society of London*, 1914. Second Edition 1924.

the surface of the water, and then, owing to the viscosity of the water, into heat energy in the water. A final state in which the corks continue to oscillate with extreme vigour while the water has almost no energy is unthinkable ; we expect a final state in which practically all the energy has found its way into the water.

" Let us examine another analogy. Let the corks be replaced by spherical lead shot, again connected by light springs, and let the system be suspended in a closed chamber containing air. After the system of shot has been started in violent oscillation let the chamber be closed up. The motion of the shot will set up waves in the air, and these will again be dissipated by viscosity. A final steady state in which the spheres continue to oscillate with high velocities for ever is again unthinkable. In point of fact, we know that the final state will be one in which the spheres are all at rest in their positions of equilibrium, or rather, to be quite precise, in which they oscillate with the infinitesimally small velocities of the Brownian movements appropriate to particles of their size ; practically all the energy will have passed from the spheres into the surrounding air."

The origin of the quantum theory. In his address * on the occasion of receiving the Nobel prize for physics Planck describes the way in which he was led to the discovery of the quantum. At that period few physicists would seem to have appreciated the fundamental importance of the unknown relation connecting the energy of radiation with its wavelength and temperature. " Planck started on Kirchhoff's idea that if he could find the emission and absorption for a single ideal radiating substance, the true radiation formula would result. He naturally worked on dynamical principles, and inevitably got a result equivalent to no result at all, for it led to the impossibilities of Rayleigh's formula. He next turned his attention to the thermodynamical aspect, and this illustrates at its best the groping process, for in fact thermodynamics does not contain the answer at all ; and yet this track guided him to the right solution. He was led to study a certain thermodynamic function (the reciprocal of the second differential of the entropy with regard to the energy!), and was struck by the fact that, with Wien's formula, it was proportional to the energy itself—a fact that is really quite accidental. For Rayleigh's formula it was proportional to the square of the energy, and Planck was happily inspired to combine the two forms into one. The result gave him the true formula. It remained to find a theory to account for it."

" In the course of his efforts to get this theory, Planck turned to the deeper meaning that is attributed to entropy on the kinetic theory, which connects it with probability, and once this was tried it gave the result

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* " Die Enstehung und bisherige Entwicklung der Quanten theorie " (Leipzig : J. A. Barth, 1920). Summarised in *Nature*, Vol. 106, p. 508 (1920).

more simply than might be expected. For in considerations of probability one is bound to work with discrete quantities, and not with continuous ; and so one must adopt the idea of atoms of energy for the calculations, though with the ultimate intention of making them infinitely small. But this intention is frustrated, because the formula is obtained without going to the limit at all. This was how Planck arrived at his theoretical explanation of the radiation formula, and by comparison with experiment he was enabled to deduce two universal constants. From the first were obtained the earliest really good values for the charge of the electron and the associated constants. The second, he confesses, perplexed him a good deal, and indeed it would have been surprising if it had not. It was the quantum."

We must now consider more in detail the development of the first form of Planck's theory, and it will first be necessary to deal with the relation between entropy and probability.

Entropy and probability. It is now established that matter is not divisible without limit but is composed of discrete molecules. In general the smallest quantity of matter which can be experimented upon contains a vast number of molecules. For example, the properties of a gas are the properties of an enormous crowd of molecules moving in all directions with widely different speeds. Again, in considering radiation in an enclosure, we are unable to deal with individual vibrations. Any natural state containing a large number of elements not in themselves measurable has been called an elemental **chaos,** and the corresponding distribution of elements **chaotic.** The observed laws of any such state are laws of averages—they are statistical relations. The ultimate state of such a system is that of maximum probability. The application of this principle to gas theory was worked out by Boltzmann (1877). He suggested a connection between the thermodynamic function known as **entropy** and the **probability** of the state.* The significance of the terms **temperature** and **entropy** is closely connected with the condition of an elemental chaos. Thus these terms cannot be applied to a single rigid atom or to a purely periodic, perfectly plane wave. In a molecular system any existing temperature differences tend to neutralise one another, the system always tends towards states of greater entropy. The statement that the entropy of the system tends to increase runs parallel to the principle that the system tends towards the more probable distribution of the elements. So we are led to the following proposition :

" The entropy of a physical system in a definite state depends solely on the probability of that state."

* This conception is discussed in greater detail in Chapter XLIII.

Expressed in mathematical form this is equivalent to saying that the entropy S is a universal function of the probability W, or $S = f(W)$.

As is shown in Chapter XLIII, p. 816, this functional equation leads to the result

$$S = k \log W.$$

The universal constant of integration k is the same for all systems, so that if its value be determined for one system it is known for all. The result may be tested by applying the equation to the known gas theory, and in this way it is found that Boltzmann's constant k is obtained by dividing the gas constant R in the equation for an ideal gas,

$$PV = RT,$$

by the number of molecules in the mass of gas considered. Thus k may be regarded as the gas constant reckoned for a single molecule.

If R refer to a gram-molecule of gas, and N be Avogadro's constant,

$$k = R/N.$$

Assuming $R = 8 \cdot 315 \times 10^7$ ergs per gram-molecule per degree C., and $N = 6 \cdot 062 \times 10^{23}$ (Millikan), we obtain for k the value $1 \cdot 372 \times 10^{-16}$ ergs per degree. C.

In thermodynamics an additive constant is left undetermined in the expression for the entropy given above.

Planck draws attention to the fundamental importance of the step by which a definite absolute value is assigned to the entropy S, when it is written in the form

$$S = k \log W.$$

" This step leads necessarily to the *hypothesis of quanta*, and moreover it also leads, as regards radiant heat, to a definite law of distribution of energy of black radiation, and as regards heat energy of bodies to Nernst's heat theorem."

The quantity W thus defined is always an integer. It may be called the **thermodynamic probability,** to distinguish it from the **mathematical probability** (a proper fraction) to which it is proportional but not equal.

Planck's resonator. With a view to simplifying as far as possible the nature and arrangement of the systems emitting and absorbing radiation Planck selected a system composed of ideal linear oscillators or resonators. Each resonator consists of two poles, charged with equal quantities of electricity of opposite sign, which may move relatively to one another on the fixed axis of the resonator. The centre of mass of each resonator is regarded as stationary. The vibration of the resonator entails one degree of freedom only. Thus, if the equipartition principle (p. 582) were applicable, each resonator would have associated with it kT units of energy which would be partly kinetic and partly potential.

It may assist the imagination to picture Planck's resonators for the

infra-red as electrically charged atoms, and for the ultra-violet as negative electrons, but it must be remembered that such atoms or electrons would possess three degrees of freedom instead of the single degree of freedom of the linear resonator. Each resonator is supposed to possess a definite natural frequency of vibration, ν.

The mean energy of a resonator. Planck considers a system of N resonators, the total energy of the system being $N\bar{U}$, where $\bar{U}$ represents the average energy of an oscillator. In order to determine the probability of the condition of the system thus defined, Planck supposes that the energy is composed of a finite number (P) of equal elements of energy ϵ so that
$$N\bar{U} = P\epsilon.$$

Any distribution of the P elements of energy amongst the N resonators is called a **complexion**. The number of possible complexions is equal to the number of ways in which P balls could be shared amongst N urns. This question is discussed more fully in Chapter XLIV, and it is found that the thermodynamic probability, W, is given by
$$W = \frac{(N+P-1)!}{(N-1)!\,P!}.$$

When N and P are very large numbers, Stirling's approximate formula $n! = n^n e^{-n}\sqrt{2\pi n}$ may be applied, and the expression for the probability assumes the form
$$W = (N+P)^{N+P}/N^N P^P.$$

The entropy of the system of resonators in thermodynamic equilibrium is accordingly given by
$$S_N = k \log W$$
$$= kN \left\{ \left(1 + \frac{P}{N}\right) \log \left(1 + \frac{P}{N}\right) - \frac{P}{N} \log \frac{P}{N} \right\}$$
$$= kN \left\{ \left(1 + \frac{\bar{U}}{\epsilon}\right) \log \left(1 + \frac{\bar{U}}{\epsilon}\right) - \frac{\bar{U}}{\epsilon} \log \frac{\bar{U}}{\epsilon} \right\}.$$

Thus the entropy of a single resonator is
$$S = k \left\{ \left(1 + \frac{\bar{U}}{\epsilon}\right) \log \left(1 + \frac{\bar{U}}{\epsilon}\right) - \frac{\bar{U}}{\epsilon} \log \frac{\bar{U}}{\epsilon} \right\}.$$

In accordance with the second law of thermodynamics,
$$\frac{dS}{d\bar{U}} = \frac{1}{T}.$$

Hence
$$\frac{1}{T} = \frac{k}{\epsilon} \left\{ \log \left(1 + \frac{\bar{U}}{\epsilon}\right) - \log \frac{\bar{U}}{\epsilon} \right\}$$

or
$$\bar{U} = \frac{\epsilon}{e^{\epsilon/kT} - 1}.$$

This then is Planck's expression for the mean energy of a resonator.

Derivation of the radiation formula. The next step in the argument is the determination of the relation between the mean energy of a resonator and the space density of the vibratory energy of the radiation. By an application of the ordinary or classical laws this relation is found to be

$$u_\nu\, d\nu = \frac{8\pi\nu^2}{c^3}\, \bar{U}\, d\nu = \frac{8\pi\nu^2}{c^3}\, \frac{\epsilon}{e^{\epsilon/kT} - 1}\, d\nu.$$

The final step involves the characteristic assumption of the quantum theory, that ϵ is not infinitesimal but is determined by

$$\epsilon = h\nu,$$

where h is an important physical quantity, known as **Planck's constant.**

Substituting this value in the above expression, the radiation formula of Planck is obtained in the form

$$u_\nu\, d\nu = \frac{8\pi h\nu^3}{c^3}\, \frac{1}{e^{h\nu/kT} - 1}\, d\nu \quad \text{(Planck)}.$$

This determines the value of u_ν, the space density of energy of uniform monochromatic unpolarised * radiation of frequency ν.

In experimental work it is more convenient to express the result in terms of the wave-length instead of the frequency, and the radiation formula then becomes

$$E_\lambda\, d\lambda = \frac{8\pi ch}{\lambda^5}\, \frac{1}{e^{ch/k\lambda T} - 1}\, d\lambda \quad \text{(Planck)}.$$

For large values of λT Planck's radiation formula becomes identical with Rayleigh's, as it reduces to the form

$$E_\lambda\, d\lambda = 8\pi kT\lambda^{-4}\, d\lambda \quad \text{(Rayleigh)}.$$

The corresponding formula, in terms of frequency, is

$$u_\nu\, d\nu = \frac{8\pi\nu^2}{c^3} \cdot kT\, d\nu \quad \text{(Rayleigh)}.$$

If, on the other hand, only small values of λT are considered, Planck's formula becomes

$$E_\lambda\, d\lambda = \frac{8\pi ch}{\lambda^5} \cdot e^{-ch/k\lambda T}\, d\lambda \quad \text{(Wien)},$$

which expresses Wien's law of energy distribution.

THE ENERGY OF LIGHT VIBRATIONS

The method of Rayleigh and Jeans. Instead of considering the mutual action between matter (or a system of resonators) and ether we may adopt the method first used by Lord Rayleigh, and later developed by Jeans and

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* The corresponding expression for plane-polarised radiation is obtained by dividing by $8\pi/c$.

Larmor, in which attention is focused on the processes occurring in a definite portion of the space through which radiation is passing. We may picture a certain volume of ether (or, if that word is objected to, of space) enclosed between perfectly reflecting walls, and imagine that the ether between them may be the seat of standing waves, which may be compared to the stationary undulations which occur in an organ pipe. We must first determine the number of independent vibrations of given wave-length in this volume, or, to speak more accurately, the number of vibrations in a small spectral region lying between λ and $\lambda + d\lambda$. Provided the wave-length is sufficiently small, this number will be very great even when the range of wave-lengths considered is small. We may assume, in general, that the number is given by $f(\lambda) d\lambda$. Now for any finite volume, v, of any homogeneous and continuous medium, $f(\lambda)$ will be proportional to v. Hence, since $f(\lambda) d\lambda$ must be a pure number, it follows from a consideration of the physical dimensions of the quantities involved that

$$f(\lambda) d\lambda = Cv\lambda^{-4} d\lambda,$$

where C is a purely numerical constant.

So we arrive at the following important proposition :

The number of independent vibrations per unit volume of a homogeneous and continuous medium of wave-length between λ and $\lambda + d\lambda$ is

$$C\lambda^{-4} d\lambda.$$

The determination of the constant C is discussed by Jeans in Chapter XVI of *The Dynamical Theory of Gases*, which deals with Statistical Mechanics in Continuous Media. It is there shown, by considering a rectangular volume of the medium, that in the case of sound vibrations in a gas $C = 4\pi$, in the case of electromagnetic radiation in free ether $C = 8\pi$, and for the vibrations of an elastic solid $C = 12\pi$. These numbers are in the ratio $1 : 2 : 3$, a result which might have been foreseen. A sound wave in a gas is determined by a single vector, namely the displacement in the direction of propagation ; in a light wave there are two independent transverse vibrations, corresponding to two planes of polarisation ; in an elastic solid waves of both kinds can coexist, there being one velocity of propagation for waves of compression and another for waves of distortion. Thus the number of vibrations for the three media under consideration must stand in the ratio $1 : 2 : 3$, already mentioned.

The principle of equipartition of energy. The principle of the equipartition of energy asserts the mean equality, as regards each degree of freedom, of the kinetic energies of translation or of rotation which are assumed in a fluid composed of an assemblage of molecules. Theoretical

and experimental results lead to the conclusion that at the same tempera-
ture the molecules of all fluids have the same mean kinetic energy of
translation, which is proportional to the absolute temperature. Let this
mean kinetic energy be denoted by $\mathbf{w}$. When n molecules of an ideal
gas are confined in a vessel of volume V, a simple application of the
principles of statistical dynamics leads to the well-known expression for
the pressure P,

$$PV = \tfrac{2}{3}n\mathbf{w}.$$

If T is the temperature on the absolute gas scale,

$$PV = RT,$$

so that

$$\tfrac{2}{3}n\mathbf{w} = RT.$$

Hence the mean molecular energy, $\mathbf{w}$, is given by

$$\mathbf{w} = \frac{3}{2}\frac{R}{n}T = \tfrac{3}{2}kT,$$

where k is the gas constant reckoned for a single molecule. In this case
each molecule has three degrees of freedom of translation so that the
principle of equipartition of kinetic energy amongst the degrees of
freedom leads to the conclusion that to each degree of freedom corresponds
an amount of kinetic energy equal to $\tfrac{1}{2}kT$. In addition to motion of
translation actual molecules may have motion of rotation. The same
principle applied to the rotation of a molecule leads to the conclusion
that to each degree of freedom of rotation which is effective, corresponds
the same amount of energy $\tfrac{1}{2}kT$. When suitably interpreted, the
principle should be applicable not only to gases but also to liquids and
solids.

In the case of a vibration, the mean kinetic energy is equal to the mean
potential energy. This is easily seen to be true by considering a
particle of mass m which is executing simple harmonic vibrations under
the action of a restoring force proportional to its displacement, q, from a
fixed point.

The equation of motion is

$$m\frac{d^2q}{dt^2} = -\mu q.$$

The first integral is the equation of energy

$$\tfrac{1}{2}m\left(\frac{dq}{dt}\right)^2 = \tfrac{1}{2}\mu(a^2 - q^2).$$

The solution of the equation is $q = a\sin\omega t$, where a is the amplitude,

and ω, the pulsatance (2π times the frequency of vibration), is given by

$$\omega = \sqrt{\frac{\mu}{m}}.$$

The mean kinetic energy is

$$\tfrac{1}{2}m\overline{\left(\frac{dq}{dt}\right)^2} = \tfrac{1}{2}m\,(a\omega)^2\,\overline{\cos^2\omega t} = \tfrac{1}{4}m\,(a\omega)^2.$$

The mean potential energy is

$$\tfrac{1}{2}\mu\overline{q^2} = \tfrac{1}{2}m\omega^2\overline{q^2} = \tfrac{1}{2}m\,(a\omega)^2\,\overline{\sin^2\omega t} = \tfrac{1}{4}m\,(a\omega)^2.$$

If then we assign to each of these equal quantities of energy the amount $\tfrac{1}{2}kT$, we find for the mean energy of the vibration the value kT.

The result may be extended to the more general case in which the energy can be expressed as a homogeneous quadratic function of the co-ordinate involved, so as to cover the case of kinetic energy, or the potential energy of small displacements from a position of equilibrium, or the energy of any type of isochronous vibration.*

Derivation of Rayleigh's formula. We are now in a position to deduce Rayleigh's formula for the distribution of energy in the normal spectrum.

Lord Rayleigh " obtained the correct value for long waves, practically by isolating in thought a rectangular block of aether, and considering all its possible modes of free vibration as excited with equipartition of energy, postulating that the natural radiation is made up of them all taken together." †

In dealing with light vibrations in free ether, the number of independent vibrations per unit volume is $8\pi\lambda^{-4}\,d\lambda$, and with each vibration must be associated, if the equipartition principle holds good, an amount of energy kT. Hence the energy density of the radiation must be

$$8\pi kT\lambda^{-4}\,d\lambda,$$

which is the radiation formula according to classical dynamics.

Various attempts have been made to obtain a radiation formula by the use of special models without departing from the classical laws, but all alike lead to the Rayleigh formula ‡ which, as we have already seen, does not agree with observation. We are forced to the conclusion that the results of the classical theory are in accord with experience only in the limiting case in which λT has large values, that is, at high temperatures or for waves of low frequency of vibration.

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* Jeans, *Dynamical Theory of Gases*, §§ 99, 100 (1921).

† Larmor, *Proc. Roy. Soc.*, Vol. 83, p. 94 (1909).

‡ See Lorentz's communication to the Solvay Conference of 1911 in " La Théorie du Rayonnement et les Quanta."

Jeans's presentation of Planck's theory. Jeans starts by assuming a result obtained in the ordinary statistical theory of gases. If ϵ denote a certain amount of energy, the probabilities that a system will have energies $0, \epsilon, 2\epsilon, \ldots$, stand in the ratio

$$1 : e^{-\epsilon/kT} : e^{-2\epsilon/kT} : \ldots , \text{ etc.}$$

If, then, we are considering a great number of vibrations, and represent by 1 the number of these vibrations possessing no energy at all, the number possessing energy ϵ will be $e^{-\epsilon/kT}$, and so on. Let the total number of vibrations be N, and suppose that M of these have zero energy. Then the number having energy ϵ is $Me^{-\epsilon/kT}$, the number having energy 2ϵ is $Me^{-2\epsilon/kT}$, and so on.

Hence the *total number*

$$N = M + Me^{-\epsilon/kT} + Me^{-2\epsilon/kT} + \ldots$$
$$= M(1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \ldots)$$
$$= \frac{M}{1 - e^{-\epsilon/kT}}.$$

The *total energy* of all these vibrations

$$= M \times 0 + \epsilon \times Me^{-\epsilon/kT} + 2\epsilon \times Me^{-2\epsilon/kT} + \ldots$$
$$= M\epsilon e^{-\epsilon/kT}[1 + 2e^{-\epsilon/kT} + 3e^{-2\epsilon/kT} + \ldots]$$
$$= \frac{M\epsilon e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})^2}.$$

Substituting for M the value previously obtained,

$$\text{the } total \text{ energy} = \frac{N\epsilon}{e^{\epsilon/kT} - 1},$$

and the *mean* energy for a single vibration $= \dfrac{\epsilon}{e^{\epsilon/kT} - 1}.$

If we now suppose that the particular vibrations concerned are those of wave-length between λ and $\lambda + d\lambda$ in a unit volume of ether, $N = 8\pi\lambda^{-4}d\lambda$, and the total energy of these vibrations is

$$E_\lambda d\lambda = 8\pi\lambda^{-4}d\lambda \frac{\epsilon}{e^{\epsilon/kT} - 1}.$$

On the classical theory the energy of a vibration may have *any* value, i.e. we must suppose the amount of energy ϵ to be infinitesimal. When ϵ approaches the value 0, the limiting value of $\dfrac{\epsilon}{e^{\epsilon/kT}-1}$ is kT, and the formula reduces to that of Rayleigh.

$$E_\lambda d\lambda = 8\pi kT\lambda^{-4} d\lambda.$$

Since this does not agree with observation, except for large values of the product λT, Planck makes the fundamental assumption of the quantum theory that ϵ, instead of being infinitesimal, is given by

$$\epsilon = h\nu,$$

where h is **Planck's constant,** and ν the number of vibrations per second.

Substituting this value for ϵ we find, for the mean energy of a single vibration, $\dfrac{h\nu}{e^{h\nu/kT}-1}$, and for the total energy of all the vibrations between λ and $\lambda + d\lambda$,

$$E_\lambda \, d\lambda = 8\pi\lambda^{-4}\, d\lambda \, \frac{h\nu}{e^{h\nu/kT}-1} = 8\pi kT\lambda^{-4}\, d\lambda \, \frac{x}{e^x-1},$$

where $x = h\nu/kT$.

Thus Planck's formula differs from Rayleigh's through the presence of the factor $\dfrac{x}{e^x-1}$.

This factor is of great importance in quantum theory and a graph of the function is shown in Fig. 278.
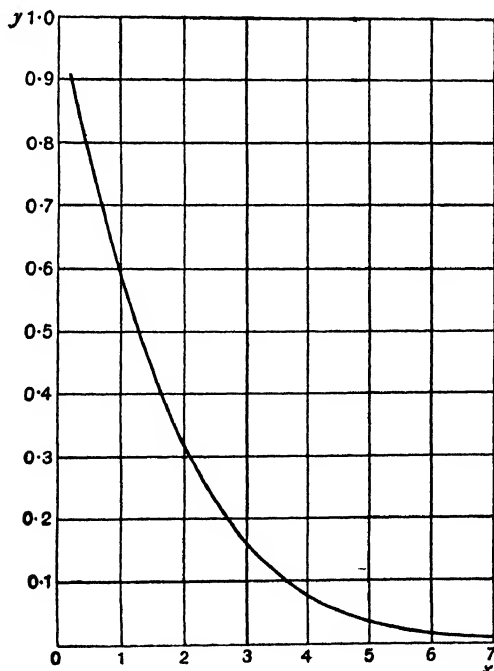
FIG. 278. GRAPH OF THE FUNCTION $x/(e^x - 1)$

The necessity for a quantum theory. The converse problem to that here considered has been discussed at length by Poincaré * and by Jeans.† If the final partition of energy in the spectrum is that given by Planck's formula, we may ask what must be the system of laws obeyed. It appears that the only hypothesis which is capable of yielding the desired result is that of discontinuities or quanta. Poincaré shows further that even if Planck's formula be regarded merely as an approximation to the true law of distribution, it is still necessary that the ultimate motion should be discontinuous. The mathematical analysis involved in the treatment of this subject is difficult, but no serious attempt appears to have been made to invalidate the proofs referred to ; and however unwilling we may feel to abandon the classical laws and the principle of equipartition, there seems to be no escape from the conclusion that the transference of energy in radiation takes place by a discontinuous process. Further, when we consider what type of discontinuities must be postulated in order to give the formula of Planck, we are led to the conclusion that the total energy of a given frequency, ν, must be made up of an integral number of units of energy determined by the relation $\epsilon = h\nu$. " In the physical system the energy of each vibration must remain the same, and equal to a multiple of $h\nu$, until a sudden cataclysm of some kind results in a change which again must be a multiple of $h\nu$ " (Jeans).

COMPARISON OF THE FORMULAE OF RAYLEIGH, WIEN AND PLANCK

It is instructive to compare the results obtained by using each of the three formulae that have been suggested for the distribution of energy in the spectrum. The comparison can be made in different ways.

Isothermal comparison. In the first place we consider an **isothermal method.** Curves can be obtained by plotting the energy against the wavelength for a constant temperature. The curves for $T = 1646°$ K. are shown in Fig. 279. In this diagram the ordinate is E_λ, and the abscissa is λ.

The values adopted for the constants are :

c (velocity of light)　　　$= 2.9977 \times 10^{10}$ cm./sec.,

h (Planck's constant)　　$= 6.56 \times 10^{-27}$ erg sec.,

k (Boltzmann's constant) $= 1.371 \times 10^{-16}$ erg/deg. C.,

whence $ch/k = 1.434$ cm. deg. C. This constant is sometimes known as c_2.

* Poincaré, *Journal de Physique*, Series 5, Vol. 2, p. 34 (Jan. 1912).

† Jeans, *Phil. Mag.*, Vol. 20, p. 943 (1910) ; *Report*, p. 33. *Dynamical Theory of Gases*, §§ 489, 491 (1921).

It may be observed from the figure that the curve obtained by Planck approximates to that of Wien for small wave-lengths, and to that of Rayleigh for long wave-lengths. This fact may also be shown from a consideration of the several formulae.

In carrying out the comparison between the formulae in an analytical way it is convenient to use the symbol x as an abbreviation for $h\nu/kT$ when using *frequencies* ν, or for $ch/k\lambda T$ when using *wave-lengths* λ. These statements are equivalent to one another since $c = \nu\lambda$.

The radiation formulae can then be written as :

$$\text{Rayleigh,} \quad E_\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\, d\lambda.$$

$$\text{Planck.} \quad E_\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\, \frac{x}{e^x - 1}\, d\lambda.$$

$$\text{Wien,} \quad E_\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\, \frac{x}{e^x}\, d\lambda.$$

Thus the formula of Planck differs from that of Rayleigh through the presence of the factor $\dfrac{x}{e^x - 1}$, and that of Wien differs through the presence of the factor $\dfrac{x}{e^x}$. It will be seen from Table 52 that for values
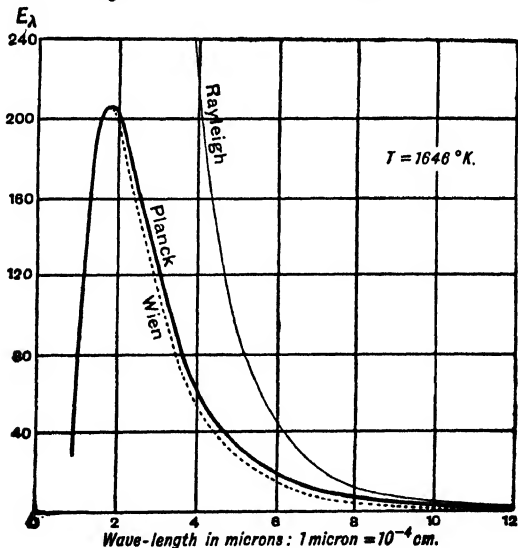
FIG. 279. CURVES FOR RADIATION FORMULAE OF RAYLEIGH, WIEN AND PLANCK

of x larger than about 2 these factors are not very different, and it is obvious on inspecting the formula that for large values of x the factors

become almost identical. On the other hand, for values of x in the region $x = 1$, and particularly for very small values, the difference is more pronounced.

TABLE 52

VALUES OF EXPONENTIAL FUNCTIONS

x	e^x	x/e^x	$x/(e^x - 1)$
0·0	1·000	0·000	1·000
0·2	1·221	0·164	0·903
0·4	1·492	0·268	0·813
0·6	1·822	0·329	0·730
0·8	2·226	0·359	0·653
1·0	2·718	0·368	0·582
1·2	3·320	0·361	0·517
1·4	4·056	0·345	0·458
1·6	4·953	0·323	0·405
1·8	6·050	0·298	0·357
2·0	7·389	0·271	0·313
3·0	20·086	0·149	0·157
4·0	54·598	0·0730	0·0764
5·0	148·41	0·0337	0·0339
6·0	404·43	0·0149	0·0149

When λT is small, that is, in the ultra-violet or at low temperatures, the value of the exponential e^x or $e^{ch/k\lambda T}$ becomes large compared with unity, and consequently the equation of Planck becomes identical with that of Wien.

When λT is large, that is, in the infra-red or at high temperatures, the value of the exponential e^x or $e^{ch/k\lambda T}$ becomes very small. In this case we may employ the approximation $e^x = 1 + x$, where x is small, and write Planck's equation in the form

$$E_\lambda d\lambda = \frac{8\pi ch}{\lambda^5} \frac{1}{\left(1 + \dfrac{ch}{k\lambda T}\right) - 1} d\lambda,$$

$$= \frac{8\pi ch}{\lambda^5} \times \frac{k\lambda T}{ch} d\lambda,$$

$$= 8\pi k T \lambda^{-4} d\lambda,$$

which is the formula of Rayleigh.

It is often desirable to study the energy distribution with regard to the wave-number instead of the wave-length. The **wave-number** $(1/\lambda)$ is the number of waves present in 1 cm., and, since $c = \nu\lambda$, it is proportional

to the frequency ν. Fig. 280 illustrates this distribution for the three formulae of Rayleigh, Wien and Planck for a temperature of 1646° K.
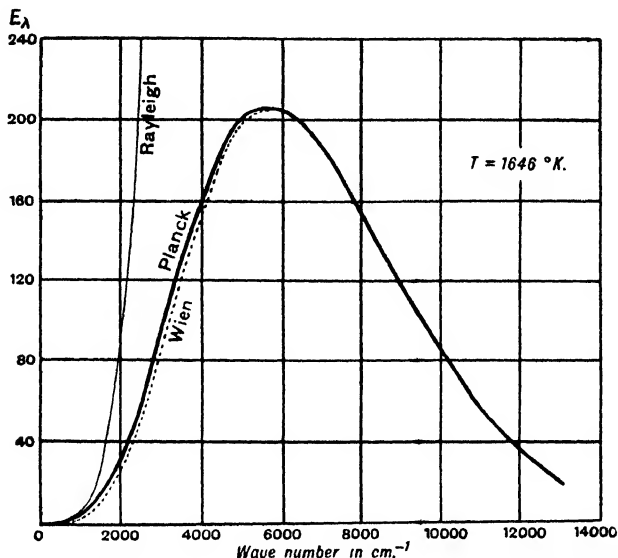
FIG. 280. ENERGY-WAVE NUMBER CURVES FOR THE FORMULAE OF RAYLEIGH, WIEN AND PLANCK

In this diagram, as in the previous one on page 769, the ordinate is E_λ, but the abscissa is the wave-number. It may be left as an exercise to plot curves showing the relation between E_ν and ν, the frequency, noticing that $\nu E_\nu = \lambda E_\lambda$.

Isochromatic comparison. Instead of plotting a radiation isothermal as in Fig. 279, an alternative plan is to plot an isochromatic curve which shows the relation between the intensity of emission and the absolute temperature for one particular wave-length. When the wave-length is shorter than 10 microns (10^{-3} cm.) the values of the energy obtained by means of the Rayleigh formula are so much greater than the experimental values or those obtained by the formulae of Wien and Planck that the comparison becomes worthless. As we approach further towards the infra-red, however, Planck's formula tends to approximate more to the formula of Rayleigh than to that of Wien for high temperatures as we have already seen above.

The energy-temperature curve for a wave-length of 10 microns is shown in Fig. 281.

Maximum values of the emissive powers at various temperatures. A more interesting comparison can be made if we calculate the wave-length

for which the emissive power is a maximum.* We shall do this for each of the three equations.

1. PLANCK'S EQUATION

Planck's equation states :

$$E_\lambda \, d\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/k\lambda T} - 1} \, d\lambda.$$
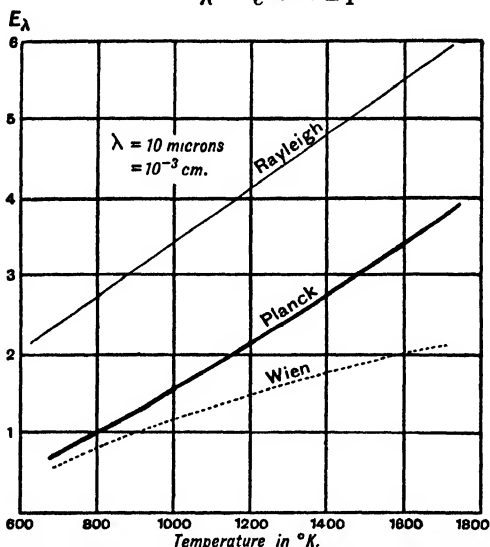
FIG. 281. ENERGY-TEMPERATURE CURVES FOR THE FORMULAE OF RAYLEIGH, WIEN AND PLANCK

If we obtain the partial differential coefficient of the energy for unit range of wave-length, E_λ, with respect to the wave-length λ, we find

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{1}{e^{ch/k\lambda T} - 1} \times \frac{-5(8\pi ch)}{\lambda^6} + \frac{8\pi ch}{\lambda^5} \times \frac{\dfrac{ch}{k\lambda^2 T} \cdot e^{\frac{ch}{k\lambda T}}}{(e^{ch/k\lambda T} - 1)^2}.$$

For a maximum value, $\dfrac{\partial E_\lambda}{\partial \lambda} = 0$, and therefore

$$-\frac{5}{\lambda} + \frac{ch}{k\lambda^2 T} \cdot \frac{e^{ch/k\lambda T}}{(e^{ch/k\lambda T} - 1)} = 0.$$

If, as before, we write $\dfrac{ch}{k\lambda T} = x$, this becomes

$$-5 + \frac{xe^x}{(e^x - 1)} = 0,$$

or

$$\tfrac{1}{5}x + e^{-x} = 1.$$

---

* Haas, *Introduction to Theoretical Physics*, Vol. II, p. 292.

. This equation has a single root given by $x = 4\cdot965$, and therefore x must be a constant. That is to say,

$$\frac{ch}{k\lambda T} = 4\cdot965.$$

Therefore the wave-length λ_{max} at which the energy per unit range of wave-length E_λ has its maximum value varies as $1/T$.

We may substitute the values for c, h and k used above, and write

$$\lambda_{max} T = \frac{ch}{k \times 4\cdot965} = b \text{ (say)};$$

$$\therefore b = \frac{2\cdot9977 \times 10^{10} \times 6\cdot56 \times 10^{-27}}{1\cdot371 \times 10^{-16} \times 4\cdot965} = 0\cdot289 \text{ cm. deg. C.}$$

The experimental measurements of Lummer and Pringsheim give a mean value of $\lambda_{max} T = b = 0\cdot2940$ cm. deg. C.

The equation, $\lambda_{max} T = b$, shows us that as the temperature increases the wave-length corresponding to maximum energy is displaced in the direction of smaller wave-lengths ; thus in the case of the visible spectrum the displacement is from the red to the violet end. This provides a theoretical explanation for the well known experimental fact that all bodies when they are heated first appear to glow with a red colour, and as the temperature rises they turn yellow and, at still higher temperatures, white. Draper first pointed out that the red glow begins to appear at the same temperature for all bodies, $525°$ C. This is confirmed by the fact that the equation, $\lambda_{max} T = b$, is quite independent of the chemical nature of the radiating body.

2. Wien's Equation

The treatment of Wien's equation is very similar. In this case we have

$$E_\lambda d\lambda = \frac{8\pi ch}{\lambda^5} e^{-\frac{ch}{k\lambda T}} d\lambda,$$

and differentiating with respect to λ, we find

$$\frac{\partial E_\lambda}{\partial \lambda} = e^{-\frac{ch}{k\lambda T}} \times \frac{-5(8\pi ch)}{\lambda^6} + \frac{8\pi ch}{\lambda^5} \times \frac{ch}{k\lambda^2 T} e^{-\frac{ch}{k\lambda T}}.$$

For a maximum value, $\dfrac{\partial E_\lambda}{\partial \lambda} = 0$;

$$\therefore -\frac{5}{\lambda} + \frac{ch}{k\lambda^2 T} = 0; \quad \therefore \frac{ch}{k\lambda T} = 5,$$

or $x = 5$, where $x = \dfrac{ch}{k\lambda T}$ as before.

We thus see that this value x only differs very slightly from the value of 4·965 obtained by using Planck's equation.

We can calculate the corresponding value of b, for we now have

$$\lambda_{max} T = \frac{ch}{k \times 5} = b;$$

$$\therefore \ b = \frac{2·9977 \times 10^{10} \times 6·56 \times 10^{-27}}{1·371 \times 10^{-16} \times 5} = 0·287 \text{ cm. deg. C.}$$

This value is very close both to that given by Planck's formula and the experimental results of Lummer and Pringsheim.

3. Rayleigh's Equation

If, lastly, we consider Rayleigh's equation, we have

$$E_\lambda d\lambda = 8\pi k T \lambda^{-4} d\lambda,$$

whence

$$\frac{\partial E_\lambda}{\partial \lambda} = -4(8\pi k T)\lambda^{-5},$$

and on putting $\dfrac{\partial E_\lambda}{\partial \lambda} = 0$, to obtain a maximum value, we can only obtain a solution on putting $T = 0$, or $\lambda = \infty$, implying either zero temperature or infinitely long wave-length. But since these conditions are at variance with the experimental results, it follows that it is necessary to reject this formula.

Summary. We may thus sum up this discussion by observing :

(1) The very close resemblance in general between the results given by the formula of Planck and that of Wien, and

(2) The very marked difference between the Rayleigh formula and the other two.

QUESTIONS

Chapter XXXIX

1. Give a short account of the origin of the Quantum Theory.

2. Derive Planck's formula for the mean energy of a resonator.

3. Discuss the principle of the equipartition of energy in the case of light vibrations, and show how it has been applied to the quantum theory of radiation.

4. Discuss the radiation formulae of Rayleigh and of Wien, and show how Planck was able to reconcile the difficulties which they encountered.

(L.U., B.Sc. Spec.)

5. Obtain an expression for the wave-length corresponding to maximum energy of emission according to the formula of Planck,

CHAPTER XL

THE SPECIFIC HEAT OF SOLIDS

THE ATOMIC HEAT OF SOLIDS

The law of Dulong and Petit. According to the well-known law of Dulong and Petit, the product of the atomic weight and the specific heat of an element is approximately constant for a number of elements. If the specific heat is expressed in calories per gram per $1°$ C., the product, which may be called the **atomic heat,** is of the order of 6 calories per gram-atom per $1°$ C. In the earlier experiments the measurements of specific heat were carried out at ordinary temperatures. Some elements which did not fall into line with the general rule gave better agreement when determinations of specific heat at higher temperatures were employed in the calculation. On the other hand, later measurements at very low temperatures have shown that as the absolute zero is approached the specific heat tends to become vanishingly small, so that the atomic heat tends to zero instead of having a finite value such as 6 calories per gram. Thus the law fails to represent the experimental results adequately when the variation of atomic heat with temperature is taken into account.

Assuming the truth of the principle of the equipartition of energy, a simple derivation of Dulong and Petit's law may be given on the basis of the kinetic molecular theory. For suppose each atom possesses n degrees of freedom. According to the theorem of equipartition each degree of freedom corresponds to an average amount of energy of vibration (half kinetic and half potential) equal to kT, where k is Boltzmann's constant. Thus the average energy of each atom is nkT, and the average energy of the gram-atom is $E = NnkT$, where N is Avogadro's constant.

The specific heat, C_v, of the gram-atom at constant volume is given by

$$C_v = \frac{dE}{dT} = Nnk.$$

But $Nk = R$, the gas constant reckoned for a gram-molecule of gas.

Hence $$C_v = nR.$$

Thus the atomic heat at constant volume is constant, provided nR is constant.

Since the value of R is known to be $1 \cdot 988$ calories ($20°$) per gram-molecule per $1°$ C., the value of n, which is necessarily an integer, must

be 3 to give agreement with the law of Dulong and Petit. This would make $C_v = 3Nk = 3R = 5.965$ calories per gram-atom or gram-molecule per $1°$ C., which is in agreement with the experimentally determined value mentioned above for the atomic heat at constant pressure. The three degrees of freedom postulated for the atom of the solid would correspond to translational motion, and it is necessary to assume that rotational motion makes no effective contribution to the specific heat in the solid state.

The suggestion that the diminution in the value of the specific heat at low temperature may be accounted for by the introduction of rigid constraints between the atoms, so as to diminish the number of degrees of freedom, is inadmissible. For solid bodies should then cease to be deformable and the compressibility ought to disappear when $T = 0$; further, as this temperature is approached the infra-red vibrations should become less and less observable, which is contrary to experience.

The measurement of specific heats at low temperatures. Since it has been observed that the law of Dulong and Petit breaks down for very low temperatures, the accurate measurement of the specific heat of substances at these temperatures has become of increasing importance in connection with theories of the solid state of matter. The principal calorimetric methods of determining specific heats have already been described in Chapters VII and VIII, but some of these may also be employed with suitable modifications to yield values at temperatures approaching the absolute zero. One of the chief difficulties in such experimental work is to secure efficient heat insulation from the surroundings, and to effect this vacuum flasks are normally used. Liquid air or liquid hydrogen may suitably be employed to reduce the temperature of the substance whose specific heat it is desired to measure.

The **method of mixtures** (p. 168) has been employed with success by Nernst, Lindemann and Koref. They cooled down the substance under test with liquid air contained in a quartz vacuum vessel. A tube open at both ends passed vertically through this vessel, and the solid was suspended on a thread inside the tube. When equilibrium of temperature had been attained the substance was lowered into the calorimeter.

The **electrical method** has been used by Nernst and Lindemann in their vacuum calorimeter (p. 181). A modification of this instrument has been designed by Simon and Lange, and is known as the **adiabatic vacuum calorimeter.** Heat losses are eliminated by surrounding the calorimeter with an enclosure which is always maintained by means of a thermostat at the same temperature as that of the calorimeter itself. For low temperature experiments the whole apparatus is immersed in liquid hydrogen contained in a Dewar flask.

Dewar has used the **method of change of state** in his liquid oxygen calorimeter, which has already been described (p. 209). In 1913 he further developed the method,* and using liquid hydrogen was able to make measurements down to a temperature as low as 20° K. He determined the mean specific heats at a temperature of about 50° K. of over fifty elements.

EINSTEIN'S THEORY OF SPECIFIC HEAT

Since the classical value, kT, for the mean energy of an atom executing linear vibrations fails to give results in accord with observation, Einstein † proposed to employ the quantum theory and substitute the value

$$kT \times \frac{x}{e^x - 1}, \quad \text{where} \quad x = \frac{h\nu}{kT}.$$

As justification for this step it may be argued that the atom, vibrating with frequency ν, must be in equilibrium with the surrounding radiation, which is assumed to obey Planck's law. When the atom is vibrating in space with three degrees of freedom, its mean energy is taken to be three times the above value, giving as the vibrational energy of the gram-atom

$$E = 3NkT \frac{x}{e^x - 1}.$$

The specific heat at constant volume is obtained by differentiating E with respect to T, giving as Einstein's expression for the atomic heat

$$C_v = \frac{dE}{dT} = 3Nk \frac{x^2 e^x}{(e^x - 1)^2}.$$

On the older view the atomic heat would have been $3Nk$, but on Einstein's theory this value is modified by the presence of the correcting factor

$$\frac{x^2 e^x}{(e^x - 1)^2}$$

which is a function of temperature. This factor varies between the value 1 for high temperatures ($x = 0$) and 0 at the absolute zero ($x = \infty$).

The shape of the curve marked E in the diagram (Fig. 282) shows C_v as a function of temperature, the ordinates giving the values of C_v and the abscissae the values of $\frac{1}{x} = \frac{kT}{h\nu} = \frac{T}{\Theta}$.

The atomic heat is zero at the absolute zero of temperature but increases as the temperature rises, finally approaching asymptotically the value $3R$ for very high temperatures.

In the ideal solid postulated by Einstein all the atoms are assumed to vibrate with the same frequency, which is a quantity characteristic of

* For a description of Dewar's liquid hydrogen calorimeter see *Dict. App. Phys.*, Vol. I, p. 55, or the original paper, *Proc. Roy. Soc.*, Vol. 89, p. 158 (1913).

† Einstein, *Ann. d. Physik*, Vol. 22, p. 180 (1907).

the particular solid considered. This frequency may be determined empirically when the value of the atomic heat is known for some temperature, which is not high enough to give approximate agreement with the law of Dulong and Petit. The value so obtained may then be employed to calculate the atomic heat for other temperatures, in order to compare the values given by the formula with those found experimentally.

Einstein tested his equation by applying it to the case of the diamond, calculating the frequency ν from the experimental value for C_p at $T = 331 \cdot 3°$ K., which was found by Weber to be $1 \cdot 84$ only. The difference between C_p and C_v is small for the diamond—though not so for other
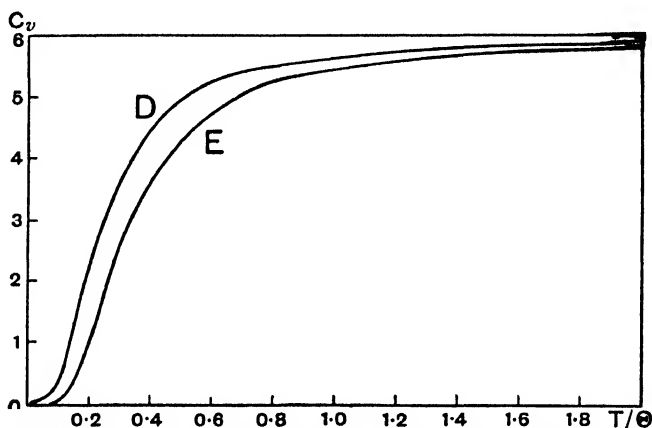
FIG. 282. EINSTEIN AND DEBYE CURVES FOR ATOMIC HEAT

substances. As far as the diamond is concerned Einstein's theory reproduces the observed values with considerable accuracy.

Certain formulae have been proposed for the determination of the characteristic atomic frequency, which have some theoretical basis though they involve an empirical constant. These will be discussed later.

Experimental measurements of the specific heat of solids, especially at low temperatures, were carried out in Nernst's laboratory from 1911 onwards,* and in the cryogenic laboratory of Onnes at Leyden. Actually it is the value of C_p, the specific heat at constant pressure, which is determined in the experiments, and from this the value of C_v must be found by employing the thermodynamic expression for the difference between the specific heats, or the simpler empirical formula

$$C_p = C_v + aT^{\frac{3}{2}},$$

where a is a constant.†

At high temperatures the atomic heat C_v approached very closely the

* See *The Theory of the Solid State*, based on lectures delivered at University College, London, by Prof. Walther Nernst (University of London Press, 1914).

† Nernst and Lindemann, *Zeitschr. Elektrochem.*, Vol. 17, p. 817 (1911).

theoretical value 5·965 calories per gram-molecule per degree, but at low temperatures there was a very marked diminution in the specific heat. Although Einstein's theory gives a general qualitative account of the observed facts, there can be no assumption of a quantitative accordance between his theory and the experimental results. Nernst and Lindemann * suggested a more complicated formula, containing two terms of the Einstein type, which gives more satisfactory agreement, but its theoretical basis is slight and it is now only of historical interest.

DEBYE'S THEORY OF SPECIFIC HEAT

In Einstein's theory it was assumed that all the atoms of the solid are vibrating with the same constant frequency which is characteristic of the substance considered. This somewhat artificial restriction was removed by Debye, who supposed that the body is characterised, not by a single frequency, but by a complete spectrum of frequencies composed of a finite number of " lines ". This number is assumed to be the same as the total number of degrees of freedom of the atoms of which the body is composed, each atom being regarded as a massive point having three degrees of freedom. The atoms of course do not vibrate independently ; the vibration of any individual atom will set neighbouring atoms in oscillation, with the result that the free vibrations of the system as a whole are the elastic solid vibrations associated with waves of distortion and waves of compression. The limitation in the number of degrees of freedom imposes a limit on the possible frequencies, and Debye assumes that no frequency can have a value greater than a certain definite maximum, ν_m, which is characteristic of the substance in question and may be expressed in terms of its elastic constants. In this way Debye obtains expressions for the total energy and the specific heat which are dependent only on a single parameter, and this may be considered either as a characteristic frequency, ν_m, or as a characteristic temperature defined by $h\nu_m/k$.

If we consider unit volume of a continuous medium through which longitudinal waves are travelling with velocity c_1, the number of independent vibrations of wave-length between λ and $\lambda + d\lambda$ is $4\pi\lambda^{-4}d\lambda$, or the number having a frequency between ν and $\nu + d\nu$ is

$$\frac{4\pi\nu^2 d\nu}{c_1^2}.$$

In the case of an elastic solid only one-third of the vibrations correspond to longitudinal waves, whilst two-thirds correspond to transverse waves. The total number of vibrations per unit volume with frequencies between ν and $\nu + d\nu$ is

$$4\pi\left(\frac{1}{c_1^3} + \frac{2}{c_2^3}\right)\nu^2 d\nu,$$

* Nernst and Lindemann, *Preuss. Akad. Wiss., Sitzungsber*, p. 347 (1911).

where c_2 is the velocity of propagation of the transverse waves of distortion. The total number of vibrations in the volume v having frequencies between ν and $\nu + d\nu$ is

$$4\pi v\left(\frac{1}{c_1{}^3}+\frac{2}{c_2{}^3}\right)\nu^2\,d\nu.$$

Debye assumes that this result holds for all values of ν from $\nu = 0$ up to a value $\nu = \nu_m$, the maximum of all the possible frequencies. Thus the total number of vibrations of all frequencies is

$$4\pi v\left(\frac{1}{c_1{}^3}+\frac{2}{c_2{}^3}\right)\int_0^{\nu_m}\nu^2\,d\nu=\frac{4\pi v}{3}\left(\frac{1}{c_1{}^3}+\frac{2}{c_2{}^3}\right),$$

But this must be the same as the total number of degrees of freedom, which is $3N$, if v denote the volume of the gram-atom. Thus ν_m is determined by the relation

$$\frac{4\pi v}{}\left(\frac{1}{c_1{}^3}+\frac{2}{c_2{}^3}\right)\nu_m{}^3=3N.$$

Hence the total number of vibrations in volume v having a frequency between ν and $\nu + d\nu$ can be expressed as $9N\dfrac{\nu^2\,d\nu}{\nu_m{}^3}$.

Debye assumes the mean energy of each vibration has the value given by the quantum theory, viz.

$$kT\times\frac{x}{e^x-1},\quad\text{where}\quad x=\frac{h\nu}{kT}.$$

Thus the total energy in volume v (one gram-atom) of the solid is

$$E=\int_0^{\nu_m}9NkT\frac{x}{e^x-1}\frac{\nu^2\,d\nu}{\nu_m{}^3}=\frac{9Nh}{\nu_m{}^3}\int_0^{\nu_m}\frac{\nu^3\,d\nu}{e^{h\nu/kT}-1},$$

or

$$E=\frac{9NkT}{x_m{}^3}\int_0^{x_m}\frac{x^3\,dx}{e^x-1},\quad\text{where}\quad x_m=\frac{h\nu_m}{kT}.$$

For each substance we may define a **characteristic temperature, Θ,** by the relation

$$\Theta=\frac{h\nu_m}{k}=\beta\nu_m,\quad\text{where}\quad\beta=\frac{h}{k}.$$

Then $x_m=\dfrac{\Theta}{T}$, and the total energy of the solid is equal to $3NkT$ (the value according to Dulong and Petit) multiplied by a factor which is a universal function of the ratio $\dfrac{\Theta}{T}$.

The atomic heat at constant volume may be derived by differentiating the expression for the energy with respect to T.

$$C=3Nk\left[\frac{12}{x_m{}^3}\int_0^{x_m}\frac{x^3\,dx}{e^x-1}-\frac{3x_m}{e^{x_m}-1}\right].$$

• The value of the atomic heat according to the law of Dulong and Petit is $3Nk$, for which we may write C_∞.

Thus $$C = C_\infty F(\Theta/T),$$

or the atomic heat is a function of the temperature T,* dependent on a single parameter, the function being the same for different elements.

The curve marked D in Fig. 282 shows the variation of atomic heat with temperature on Debye's theory for comparison with Einstein's theory.

Approximate formulae for the calculation of C for both large and small values of x_m are given in Debye's paper, and a table giving numerical values of C in relation to x_m has been published by W. Nernst.† The curve obtained by Debye for aluminium, copper and silver is shown in Fig. 283. The abscissa represents T/Θ and the ordinate $F(\Theta/T)$.
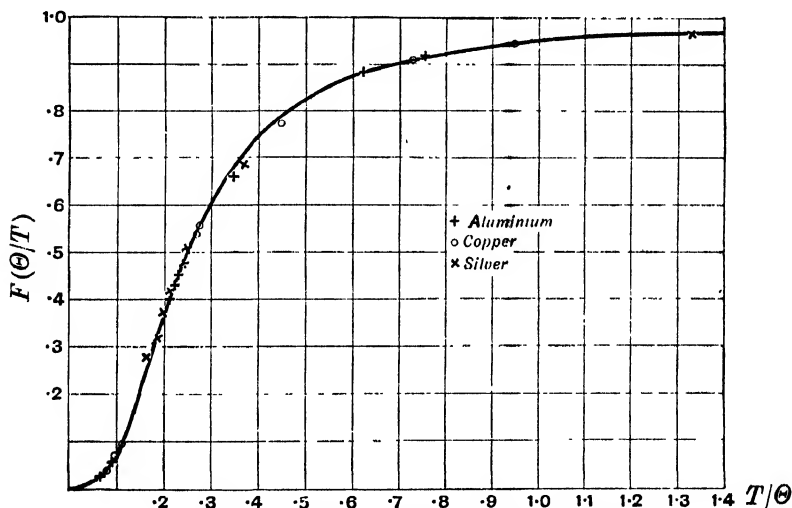
FIG. 283. DEBYE'S CURVE FOR SPECIFIC HEAT

Large values of x corresponding to low temperatures. This corresponds to the case when the temperature is low. In the expression

$$\frac{C}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{x^3\,dx}{e^x - 1} - \frac{3x}{e^x - 1},$$

* Incidentally it may be noticed that we might conform to the spirit of the quantum theory by expressing temperature on the absolute scale as a frequency. The product of the absolute temperature and Boltzmann's constant represents a certain amount of energy, and this may be regarded as equivalent to a quantity of energy $h\nu$, so that $kT = h\nu$ where ν is a frequency corresponding to, or serving as a measure of, the particular temperature T.

† *Die theoretischen Grundlagen und experimentellen des neuen Warmesatzes*, W. Knapp, Halle (1918).

the second term vanishes for large values of x and in the integral we may substitute ∞ for the upper limit, and so obtain

$$\frac{C}{C_\infty} = \frac{12}{x^3} \int_0^\infty \frac{x^3\,dx}{e^x-1} = \frac{12}{x^3} \times \frac{\pi^4}{15} = \frac{4}{5}\pi^4 \frac{T^3}{\Theta^3} = 77 \cdot 938 \frac{T^3}{\Theta^3}$$

Thus at very low temperatures the specific heat is proportional to the third power of the absolute temperature.

Debye's expression for the characteristic frequency in terms of the elastic constants. In Debye's theory the characteristic frequency ν_m is determined by the equation

$$\frac{4\pi v}{3}\left(\frac{1}{c_1^3} + \frac{2}{c_2^3}\right)\nu_m^3 = 3N,$$

where c_1 is the velocity of waves of compression, c_2 the velocity of waves of distortion. These velocities may be expressed in terms of the elastic constants of the substance. We find in fact from the theory of elasticity

$$c_1 = \sqrt{\frac{3(1-\sigma)}{(1+\sigma)K\rho}}, \quad \text{and} \quad c_2 = \sqrt{\frac{3(1-2\sigma)}{2(1+\sigma)K\rho}},$$

where ρ is the density, K the compressibility, and σ Poisson's ratio (the ratio of the lateral contraction to the longitudinal extension).

Hence the maximum frequency which limits abruptly, according to Debye's theory, the range of vibrations forming the " spectrum " of the solid is given by

$$\nu_m = \left(\frac{3N}{vF}\right)^{\frac{1}{3}}.$$

where

$$F = \frac{4\pi}{3}\rho^{\frac{3}{2}}K^{\frac{3}{2}}\left[2\left(\frac{2(1+\sigma)}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \left(\frac{1+\sigma}{3(1-\sigma)}\right)^{\frac{3}{2}}\right].$$

It should be noticed that this formula for the frequency contains no undetermined constant; all the quantities involved can be measured experimentally. In the case of aluminium and silver, Debye found that the frequency calculated in this way agreed within about one per cent. with that from the specific heat, in the case of copper there was a difference of about 6 per cent., in the case of lead about 20 per cent. between the two values. It must be remembered, however, that the determinations were made by different observers on different specimens of material, and as the elastic properties depend to a marked degree on the purity of the specimen and the treatment it has received, the agreement is really remarkable.

Numerical values for the characteristic temperature. Later values of the Debye characteristic temperature Θ from measurements of specific heat at low temperatures are for several elements in fair agreement with

those obtained from the elastic constants of the metal in bulk. The values for copper, silver and gold are as follows :

	Cu	Ag	Au
From specific heat -	- 316·23	215	170
From elastic constants	- 325	215	161

From a knowledge of the characteristic temperature the characteristic frequency can be calculated by means of the equation $\Theta = \beta \nu_m$, where $\beta = h/k$. Assuming that $h = 6·547 \times 10^{-27}$ erg sec. and $k = 1·3708_9 \times 10^{-16}$ erg deg.$^{-1}$, we find $\beta = 4·776 \times 10^{-11}$ deg. sec. For example, taking Θ for silver as $215°$, the characteristic frequency is found to be $4·50 \times 10^{12}$ sec^{-1}.

THE THEORY OF BORN AND KÁRMÁN

In Debye's theory of specific heat the solid is regarded as a continuum, as in the ordinary theory of elasticity. Actually a solid is composed of a very large number of discrete particles which are held together by the forces of cohesion. In a single crystal the geometrical form must be attributed to the orderly arrangement of these particles. Crystallographers have long been familiar with the theory of such regular arrangements of points in space, and the work of Sir William Bragg, Prof. W. L. Bragg and others on the structure of crystals by the method of X-ray analysis has fully confirmed the expectations derived from theory.

Born and Kármán considered the case of a crystal extending to infinity in all directions and sought to determine the law according to which the natural vibrations are distributed amongst the separate frequency regions. If the fundamental group in an elementary cell consists of s different particles, it is found that there will be $3s$ natural vibrations when an elastic wave of given wave-length travels through the crystal in some definite direction. The first three frequencies correspond to the ordinary acoustic vibrations of the crystal. The expression for the thermal capacity is built up of 3 Debye functions and a series of Einstein functions corresponding to $3(s-1)$ monochromatic vibrations.

The calculations are complicated and the experimental verification of the theory is difficult, but on the whole satisfactory agreement has been found between the modern form of the theory and the experimental results.

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Mott and Jones, *The Properties of Metals and Alloys* (1936).

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QUESTIONS

Chapter XL

1. Describe experiments that have been made upon the specific heat of substances at low temperatures and discuss the results obtained.

(Camb. Part II Tripos)

2. Write an account of the measurement of specific heats at low temperatures. Discuss briefly the law of Dulong and Petit.   (L.U., B.Sc)

3. Write a short account of the specific heats of solids in relation to temperature, and discuss, in some detail, any theory which has been proposed to explain the facts.   (St. A. U.)

4. Write an account of Debye's theory of the specific heat of an isotropic solid, and show that on this theory the specific heat at extremely low temperatures varies as the cube of the absolute temperature.   (L.U., M.A. Hons.)

5. Describe one of the methods by which the specific heats of materials have been investigated at temperatures of the order of 10° or 20° absolute.   Give a general account of the results obtained.   (L.U., B.Sc.)

STATISTICAL METHODS AND PROBABILITY

Statistical methods in physics. Since the seventeenth century the attempt has been made to explain physical phenomena in terms of dynamical principles. Thus Huygens, in 1680, wrote: " In true philosophy we should conceive the cause of all natural phenomena in terms of mechanics. This we must do, or for ever renounce the hope of understanding anything of Physics." But in certain regions dynamical principles have proved insufficient for the interpretation of observed phenomena. A noteworthy case is found in the realm of thermodynamics. The first law, expressing the equivalence of heat and work, is an illustration of the way in which mechanical ideas may be extended to include other branches of physics. But the second law, as Boltzmann showed, is not based merely on dynamics; it involves the calculus of probabilities. The occurrence of statistical results in heat seems natural when we reflect that the temperature of a gas is a measure of the *average* energy of molecules. Pressure again is a measure of the *average* rate of change of momentum of the molecules when colliding with the walls of the containing vessel. Boltzmann came to the conclusion that the thermodynamical function called **entropy,** which may be employed in stating the second law, **was connected with the probability** of the state under consideration. In work connected with quantum theory, statistical methods have again been invoked, and many of the investigations have involved considerations of probability. Even in wave mechanics, which at first promised to give a representation of the behaviour of electrons and protons capable of visualisation, it seems necessary to regard the wave equation as the expression of a mathematical probability.

It is desirable to consider these statistical methods in some detail, beginning with quite elementary considerations.

The abstract nature of mathematical concepts. Mathematics deals with abstractions. This has been emphasised by A. N. Whitehead in *Science and the Modern World* (p. 29) :

" Abstract ideas which to us are immediately obvious must have been for them [men in primitive societies], matters only of the most dim

apprehension. For example take the question of number. We think of the number ' five ' as applying to appropriate groups of any entities whatsoever—to five fishes, five children, five apples, five days. Thus in considering the relations of the number ' five ' to the number ' three ', we are thinking of two groups of things, one with five members and the other with three members. But we are entirely abstracting from any consideration of any particular entities, or even of any particular sorts of entities, which go to make up the membership of either of the two groups. We are merely thinking of those relationships-between those two groups which are entirely independent of the individual essences of any of the members of either group. This is a very remarkable feat of abstraction ; and it must have taken ages for the human race to rise to it. During a long period, groups of fishes will have been compared to each other in respect of their multiplicity, and groups of days to each other. But the first man who noticed the analogy between a group of seven fishes and a group of seven days made a notable advance in the history of thought. He was the first man who entertained a concept belonging to the science of pure mathematics."

As a further illustration of the abstract nature of a mathematical statement let us consider the apparently simple sentence ONE AND ONE MAKE TWO. Assuming that this is more than a mere definition of the word TWO, we may ask, " is the statement always true " ? The amoeba is one of the simplest forms of animal life and it reproduces its kind by fission. Again two amoebae are sometimes observed to flow together and fuse into a single organism. Perhaps the mathematician may object that it is not legitimate to make tests on living creatures—they may not be subject to the *laws* of arithmetic. Let us then make another test. An electron is introduced into a box, and shortly afterwards another electron is placed in the same box. Surely in this case there must be two electrons in the box. But since the discovery of a positive electron (or positron) in 1932 there is the possibility that one electron may have been negative, the other positive, and the experimenter may have found on adding one to one, no electron at all, but only a flash of radiation. Or consider a shell filled with high explosive, moving to the east, colliding with a similar shell moving to the west. As a result of the encounter we find only small solid fragments and clouds of gas. Such examples show that we must exercise caution in applying mathematical results, and in the particular arithmetical statement cited some qualifying clause is needed, such as " One and one make two, provided the entities concerned are permanent, and do not interact with one another".

In physics we often meet with instances where so-called " laws " are only true when certain conditions are satisfied. An excellent example of the kind is afforded by Dalton's law of partial presssures. According to this law the pressure of a mixture of gases on the walls of the containing vessel is equal to the sum of the " partial pressures ", that is, the pressures which the constituents would exert if each occupied the vessel separately. *But the law is only true provided the gases have no chemical action on each other*. We know that the kinetic theory of gases gives a simple explana-

tion of the law, attributing the resultant pressure to a summation effect arising from the joint action of the separate molecules. Any departure from the law is attributed to the chemical actions between the molecules, such interaction resulting in a change in the entities (physical molecules) which produce the pressure.

So we see how important it is in all statistical investigations to be on our guard against implicit assumptions, such as the assumption that the individuals concerned have no influence upon one another, for these may involve some change in the conditions of the problem. The opinion that " figures can prove anything " receives a certain measure of support from such considerations.

Probability. We turn to the examination of the meaning of **probability,** a subject which has attracted much attention not only in connection with statistical theories but also in wave mechanics. Eddington * has pointed out that the word " probability " is used with more than one meaning, and as has happened in many other cases confusion has resulted. A notable instance is the use of the word " force " with two distinct meanings in the early development of Dynamics.

" When a word in everyday use is adopted as an exact scientific term it does not always retain its everyday meaning. For example, in mechanics *work* is a technical term having a meaning by no means coextensive with our ordinary notion of work. Scientifically no work is done unless something is moved. The acrobat who stands at the base of a tableau, with the other members of the troupe supported gracefully on his shoulders, does no work. Similarly it must not be expected that probability when used as an exact term in mathematics and physics will retain all the shades of meaning that it may have in ordinary conversation. As a technical scientific term it denotes something to which a definite numerical measure can be attributed ; to secure this definiteness we must sacrifice some of the looser implications of probability."

In making a statement such as " The probability is $\frac{1}{6}$ that my next throw with the dice will be an ace ", we are dealing with what is sometimes called the *a priori* probability. " Verbally the statement refers to a particular event ; but its meaning refers to a class of events of which the particular event is one member. Thus numerical probability is a communal property, acquired through membership of a class."

The idea of numerical probability is closely associated with, if not actually derived from, games of chance, as in tossing a coin or in throwing dice. But the mathematician makes an abstraction from all such material structures as coins, cards or dice. For him an **aspect** is nothing material but a word used as a symbol to denote a distinctive state or condition. A simple illustration suitable for the lecture room may be of

* Eddington, *New Pathways in Science* (1935), p. 110.

assistance in understanding this point of view. Consider the process of placing a square lantern slide in its carrier in the darkened room. Let us suppose that one face of the slide has been slightly roughened, so that the lantern operator knows which face to put next to the condenser From the standpoint of the audience the resulting picture on the screen may have one of four aspects, the sky may be to the right or to the left, it may be to the bottom or to the top. Assuming that the operator has no other previous information as to the way in which the slide should be inserted, there is only one chance in four of the picture being the right way up, that is, of the desired aspect being achieved as the result of the operation.

If, however, the operator cannot distinguish between the two faces of the slide there will be eight possible ways of inserting the slide and eight possible aspects. For instance, a slide illustrating a printed page may give a picture the right way up, but the lettering may be reversed through lateral inversion of the image. This makes the number of possible aspects twice as great as in the former case.

Parenthetically it may be remarked that a number of interesting illustrations of probability may be obtained by means of lantern slides. Thus a single arrow marked on a slide may appear to have one of the four aspects $\leftarrow \rightarrow \downarrow \uparrow$. In this instance lateral inversion of the image would not be observed because of the symmetry of the figure. Again, a set of slides may be prepared of different colours, or marked like the faces of dice, or with a series of geometrical figures. Such a set may be placed in a box and a single slide be drawn by chance for exhibition in the lantern.

Mathematical definition of probability. We begin with a definition : " When a certain aspect is possible in a ways, and is not possible in b ways, then the probability of the aspect occurring is $a/(a+b)$." Thus, to borrow the phraseology of Newton : " Mathematical, true, or absolute " probability is defined as the ratio of a certain number of aspects (namely those which are possibly observable) to the total number of aspects included in the class.*

This must be regarded as a *definition* of numerical probability, for it implies that all the $a+b$ aspects have " the same chance of appearing ", that is to say, so far as our knowledge of the problem goes there is no condition which favours one aspect rather than another. It must be noticed that the *total* number of aspects depends on the information in the possession of the observer.

This form of definition is in agreement with the more familiar expression found in mathematical text-books. " If an event can occur in a

* When b is zero, and the value of the ratio $a/(a+b)$ is unity, the probability becomes a certainty.

ways, and can fail in b ways, then the probability of its occurring is $\dfrac{a}{a+b}$, and the probability of its failing is $\dfrac{b}{a+b}$."

In such a case the $a+b$ ways are *assumed* to have each the same chance of occurrence.

The sum of the two probabilities is $\dfrac{a}{a+b} + \dfrac{b}{a+b} = 1$, corresponding to " certainty ", since the event must either happen or fail.

This method of regarding probability, in which it is treated as a mathematical abstraction, does away with the difficulty frequently met with by those who attempt to *test* the statement by experiment.* Such experiments may *suggest* the adoption of the definition already given but can never prove its truth or necessity. All the experiments can do is to show to what degree the material apparatus employed (coins or dice) conforms to the hypothesis which may be described as " equality of opportunity ". Has the coin two heads, or two tails? Are the dice loaded so that one face tends to occur more frequently than the definition would lead us to expect?

Mrs. Weldon " four times recorded the result of 4,096 throws of dice, showing that the faces with more than three points were, on the average, uppermost slightly more often than was to be expected ". The interesting explanation is " that the points on dice are marked by little holes scooped out of the faces, and that the points 6, 5, and 4, respectively opposite 1, 2, and 3 are somewhat lighter, more of the ivory having been removed ". (From Sir Edward Poulton's Presidential Address to the British Association in 1937.)

Calculus of probabilities; independent events. It is important to extend the theory so as to include the occurrence of *independent* events. What is the probability of two independent events *both* occurring? The answer to this question is that the probability is measured by the *product* of the two separate probabilities. We shall illustrate this statement by some simple examples, but first it is necessary to insist that emphasis must be put on the word " independent ". Many of the difficulties arising in problems of probability are due to want of knowledge—a want which may be either partial or complete—about the " independence " of the events under consideration.

On tossing or spinning a single coin there are two **possible aspects** that may be presented by the fallen coin, a " head " or a " tail ", and it may be regarded as axiomatic that after making a large number of throws the ratio of the number of heads to the number of tails is nearly unity.

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* " Sometimes actual trial seems to throw discredit on the mathematical measure of a chance " (Chambers). Such " failure " is often attributed to the number of trials being too small. But what is a " small " number in this connection?

This means that for a normal coin the statement commends itself to general acceptance, and accordingly we assert that the **probability** for each event is $\frac{1}{2}$. Let us consider some simple cases.

Two unlike coins. Suppose we toss a copper coin (penny) and a silver coin (florin), which we may call coin " 1 " and coin " 2 "; four **complexions** are possible:

Complexion	Copper coin, No. 1	Silver coin, No. 2	Symbol	Probability
(1)	Head	Head	$a_1 a_2$	1/4
(2)	Tail	Tail	$b_1 b_2$	1/4
(3)	Head	Tail	$a_1 b_2$	1/4
(4)	Tail	Head	$b_1 a_2$	1/4

Here a stands for head, b for tail, a_1 means that a head is shown by coin 1, b_2 means that a tail is shown by coin 2, etc.

The possible events or complexions are represented by terms of the product

$$(a_1 + b_1)(a_2 + b_2).$$

The events are independent, and the probability of each of the four complexions is 1/4.

We notice that the probability of a composite event, such as $a_1 a_2$, is the product of the probabilities of the individual component events, a_1 and a_2.

Two similar coins. When the coins cannot be distinguished from each other, as in the case of two similar copper coins (two pennies), complexions (3) and (4) can no longer be distinguished, and must be regarded as identical, so that now there are only **three statistical states.**

The events are now represented by terms of the binomial expression

$$(a + b)^2 = a^2 + 2ab + b^2.$$

The probability of a^2 or b^2 is 1/4, but that of ab is twice that of a^2 and b^2, that is 1/2.

It is to be noticed that the probability is greatest for the state showing as many heads as tails.

The following table summarises the results:

Two similar coins.

Statistical state		Symbol	Weight		Probability
(1)	Both heads - -	a^2	(one complexion)	1	1/4
(2)	Both tails - -	b^2	(one complexion)	1	1/4
(3)	One head and one tail	ab	(two complexions)	2	2/4

.The term **weight** is applied to the number of complexions in any assigned statistical state.

We consider next the case of three coins.

Three unlike coins.   There are eight complexions, all equally probable.

Complexion	No. 1		No. 2		No. 3		Symbol
(1)	Head	a	Head	a	Head	a	$a_1a_2a_3$
(2)	Head	a	Head	a	Tail	b	$a_1a_2b_3$
(3)	Head	a	Tail	b	Head	a	$a_1b_2a_3$
(4)	Head	a	Tail	b	Tail	b	$a_1b_2b_3$
(5)	Tail	b	Head	a	Head	a	$b_1a_2a_3$
(6)	Tail	b	Head	a	Tail	b	$b_1a_2b_3$
(7)	Tail	b	Tail	b	Head	a	$b_1b_2a_3$
(8)	Tail	b	Tail	b	Tail	b	$b_1b_2b_3$

The possible complexions are represented by terms of the product

$$(a_1+b_1)(a_2+b_2)(a_3+b_3).$$

All complexions are equally probable, the probability of an assigned complexion being $1/8$.

Three similar coins.

There are four statistical states, namely

Statistical state	Symbol	Weight		Prob-ability
(1) All heads -	a^3	(One complexion)	1	$1/8$
(2) All tails - -	b^3	(One complexion)	1	$1/8$
(3) Two heads and one tail	a^2b	(Three complexions)	3	$3/8$
(4) One head and two tails	ab^2	(Three complexions)	3	$3/8$

The events are represented by terms of the product $(a+b)^3$.

Again, the probability is greatest for those states showing the nearest approach to equality between heads and tails.

Any number of coins, n (say).   First suppose the coins are all unlike. The possible complexions are represented by terms of the product

$$(a_1+b_1)(a_2+b_2) \ldots (a_n+b_n).$$

When the n coins are identical, the possible combinations are given by the terms of the binomial expansion

$$(a+b)^n = a^n + na^{n-1}b + \frac{n(n-1)}{1\cdot2}a^{n-2}b^2 + \ldots + b^n,$$

$$= a^n + {}^nC_1a^{n-1}b + {}^nC_2a^{n-2}b^2 + \ldots + b^n,$$

where ^nC_r denotes the number of combinations of n things r at a time. The statistical states are represented by

$$a^n, \ a^{n-1}b, \ a^{n-2}b^2, \ldots, \ a^r b^s, \ldots b^n.$$

Here $a^r b^s$ means that we have r heads and s tails, where $s = n - r$.

The **weight** or **possibility number**, the number of different complexions within the statistical state, is denoted by P and is equal to the number of combinations of n things r at a time, that is,

$$P = {}^nC_r = \frac{n!}{r! \, s!}.$$

Here the symbol $n!$ denotes " factorial n ", that is,

$$n(n-1)(n-2) \ldots 3 . 2 . 1.$$

The *total* number of different complexions is $\Sigma {}^nC_r$, where the summation represented by the symbol Σ extends from $r = 1$ to $r = n$.

The **mathematical probability** W of the combination $a^r b^s$ is found by dividing the possibility number by the total number.

that is,
$$W = \frac{{}^nC_r}{\Sigma {}^nC_r} = \frac{\dfrac{n!}{r! \, s!}}{2^n},$$

since
$$\Sigma {}^nC_r = (1 + 1)^n = 2^n.$$

Combination having the maximum probability. To find which combination of heads and tails is most likely in a large number of throws we must calculate the maximum value of W or of ^nC_r.

It is shown in books on algebra that, when n is even, the value of ^nC_r is greatest when $r = \dfrac{n}{2}$, or, remembering that s is defined as $n - r$, when $r = s$.

Thus the probability is a maximum for the state in which there are as many heads as tails. We call the maximum value of the probability $W_{\max}$.

In this case
$$W_{\max} = \frac{n!}{\ldots} \times \frac{1}{2^n}.$$

We now consider a state which does not *exactly* correspond to this maximum value of W. Instead of having $r = s = \dfrac{n}{2}$, let us suppose that

$$r = \frac{n}{2} + \epsilon, \quad \text{and} \quad s = \frac{n}{2} - \epsilon.$$

We call W_x the value of the probability corresponding to this combination.

Then
$$W_x = \frac{n!}{\left(\frac{n}{2}+\epsilon\right)!\left(\frac{n}{2}-\epsilon\right)!} \times \frac{1}{2^n}.$$

Hence
$$\frac{W_x}{W_{\max}} = \frac{\left(\frac{n}{2}!\right)^2}{\left(\frac{n}{2}+\epsilon\right)!\left(\frac{n}{2}-\epsilon\right)!}.$$

When n is a large number this may be expressed in a more convenient form by employing Stirling's theorem.

Stirling's theorem. Early in the eighteenth century the Scottish mathematician James Stirling (1693-1770), a friend of Colin Maclaurin, enunciated a famous theorem, which enables us to give a fairly simple expression for $\log_e n!$ when n is large. This may be written

$$\log n! \simeq n \log n - n + \tfrac{1}{2}\log(2\pi n).$$

For sufficiently large numbers

$$\log n! \simeq n \log n - n.$$

With the aid of Stirling's theorem we find

$$\frac{W_x}{W_{\max}} = e^{-\frac{2\epsilon^2}{n}}.$$

The form of this exponential expression is noteworthy, as it occurs frequently in statistical problems. We shall meet with the function $y = e^{-x^2}$ later in the Gaussian law of errors.

This result may be extended without much difficulty to particles having a large number of possible states. A coin has only two possible states, a " head " and a " tail ", but the ivory cube used in the game of dice has six sides and six possible states.

Still more complicated cases may be imagined. One way of illustrating such a problem is to take a board with p square cells arranged side by side and then to throw into these cells from a great distance N balls. We may suppose that n_r balls are found in cell a_r, etc., where $\Sigma n_r = N$. The " possibility number " is $P = \frac{N!}{\Pi n_r!}$, where the symbol Π represents the *product* of the factorials typified by $n_r!$.

The mathematical probability $W = \frac{P}{\Sigma P} = \frac{N!}{\Pi n_r!}\left(\frac{1}{p}\right)^N$, where p is the number of cells in the board.

An expression of this type is met with in the more advanced treatment of statistical mechanics.

THE THEORY OF ERRORS

The marksman and the target. We now turn to a type of probability of a different kind. This arises in connection with the so-called Theory of Errors, and is of great importance in all classes of scientific work in which measurement is possible or statistical methods can be applied.

A simple illustration of this type of probability occurs when a marksman consistently tries to make his hits at the centre of the target. Suppose that after firing twenty rounds he has hit the bull's-eye twice, it is legitimate to surmise that in subsequent firing he is likely to hit the centre of the target once in every ten rounds, or the probability of his hitting the centre is one in ten. Thus the **probability** is defined as the value of the ratio :

$$\frac{\text{number of times an event occurs}}{\text{total number of possible occurrences}}.$$

This statement as to the probability assumes that *all the conditions remain exactly the same*. Any individual shot may be affected by the wind, by the pressure or temperature of the atmosphere, by the physical condition of the marksman, by the nature of the ammunition, and so forth. Consequently the " target diagram " will show a number of spots which cluster round the central point.

By increasing the number of shots, so that all possible conditions are included, the numerical value of the probability may be made more reliable.

In such a test the marksman must consistently endeavour to eliminate so far as is possible all elements of chance, although it is impossible for him to eradicate them completely. This is the characteristic feature of the second type of probability.

Other illustrations are afforded by an astronomer who seeks to determine the mean distance of the earth from the sun, or by a physicist who wishes to find an accurate value of the mechanical equivalent of heat. Birge * made a series of 500 cross-hair settings on a very wide but symmetrical solar spectrum line, under conditions as favourable as possible to equal reliability for all observations. In such problems the " correct " value of the sought quantity is unknown, and the arithmetic mean is usually adopted as the most probable value. This procedure assumes the absence of **systematic errors** due to some cause making the observed results consistently either too high or too low. The errors considered are supposed to be **accidental**, being governed by chance alone.

* Birge, *Phys. Rev.*, Vol. 40, p. 207 (1932).

The normal law of error. The law of frequency of error when the number of cases considered is large is often called the Gaussian law of error, though it was discovered by Laplace. Let x be the magnitude of an error and y the frequency of its occurrence, that is, its probability. Then the law of error expresses the way in which x and y are connected, or gives y as a function of x. It is shown in mathematical works* that a suitable form in many cases is represented by

$$y = ke^{-a^2x^2},$$

where e is the base of the Napierian logarithms and k and a are numerical factors. This mathematical formula is obtained by replacing a sum of a large number of small terms by an integral.

There has been much discussion as to the validity of the proposed proofs of the Gaussian error law, but according to Whittaker and Robinson : " Theory asserts, and observation confirms the assertion, that the normal law is to be expected in a very great number of frequency distributions, but not in all."

The Gaussian error law should be followed, provided the errors are purely " accidental ", that is to say, are governed by chance alone. They must not be systematic or constant, as would be the case if some cause were acting tending to produce deviation always in the same direction. Further conditions are that the errors are equally liable to be positive (making the result too large, say) or negative (making the result too small), and are more likely to be small than large, with very large errors entirely lacking. These conditions imply that the number of cases considered is extremely great.

The probability function and the probability curve. In its simplest form this function may be written $y = e^{-x^2}$, and the graph possesses definite features which are consistent with the facts mentioned above. Thus

(1) The graph is symmetrical with respect to the axis of y, the frequency being the same for positive or negative equal values of x.

(2) The graph passes through a maximum for $x = 0$.

(3) As x increases numerically, y decreases and becomes vanishingly small when x becomes large.

From the definition of probability given on p. 794, it follows that the area of a narrow strip of the figure between x and $x + \delta x$ is proportional to the number of events (or observations) associated with an error of magnitude x.

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* A simple treatment of the probability function is given by Gheury de Bray in *Exponentials made Easy* (Macmillan). For applications see Whittaker and Robinson, *The Calculus of Observations* (Blackie). In this book prominence is given to arithmetical, as distinguished from graphical, methods.

The diagrams (Figs. 284 and 285), reproduced from *Exponentials Made Easy*, show various forms of the probability curve, $y = ke^{-a^2x^2}$. In the first
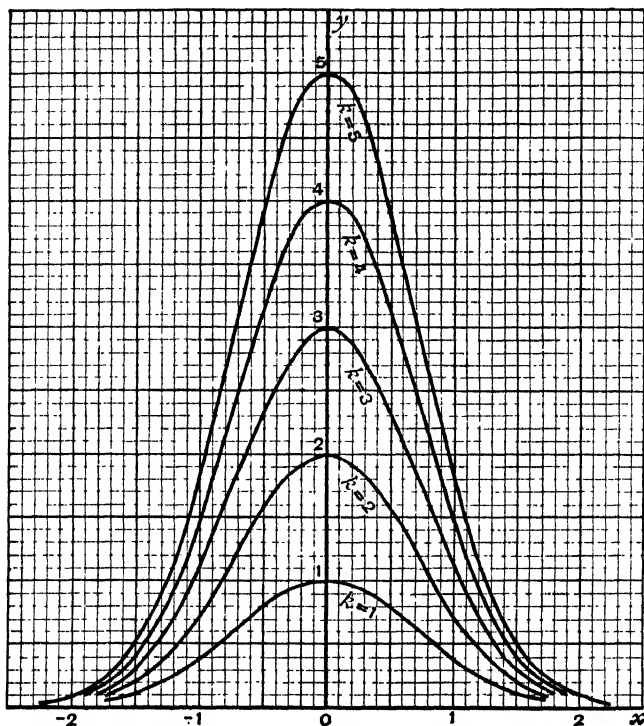
FIG. 284. PROBABILITY CURVES FOR DIFFERENT VALUES OF k

diagram we take $a = 1$ and give k values 1, 2, 3, 4, etc. These are the values of the ordinate at $x = 0$, and give the probable frequency of zero error. The greater the probability of very small errors the higher will
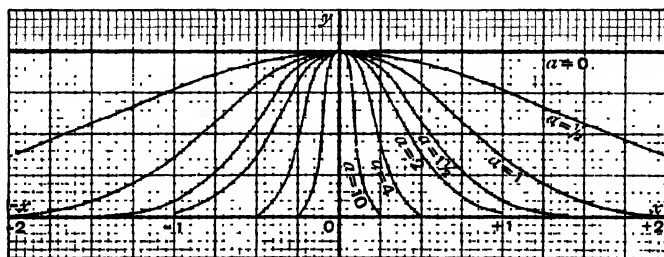
FIG. 285. PROBABILITY CURVES FOR DIFFERENT VALUES OF a

be the peak of the curve. These curves are all copies of the same curve to a different scale of y.

In Fig. 285 we take $k = 1$ and give a values 1, 2, 3, 4, etc., and in this way we obtain curves which are all different. The quantity a is called the **accuracy modulus,** or the **modulus of precision,** because as a increases the precision of the measurements increases. This means that the curve becomes more " peaked ", corresponding to a greater proportion of small errors.

The **normal law of error** may be represented by a particular case of the general equation, namely

$$y = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2}.$$

This is the equation of a curve known as the **standard normal figure.** In this case $a = 1/\sqrt{2}$.

The area of the complete figure is unity, and the length of the central ordinate is approximately 0·3989. The values $x = -0·6745$ and $x = +0·6745$ are known as the quartile values of x. The ordinates drawn through these points bisect the portions of the figure to the left and to the right of the central ordinate.

Applications of the law of error. The law of error is of importance in many branches of enquiry in natural science and in economics. Not only may it be applied to the errors made in the determination of a physical constant, but it is of value in such problems as the measurement of the ability of candidates by means of marks in an examination. In botany and zoology the statistical study of living organisms has been called **biometrics,** and through the work of Galton, Pearson and others this study has thrown much light on questions of variation and heredity.

Again, in the subject of anthropometry when measurements are made of the height or weight of a group of men, we obtain a Gaussian distribution, provided that the group is sufficiently large in number, and that what is termed " random sampling " of the general population is attained. Further, insurance companies base their actuarial calculations of expectation of life on the law of error. " Both in physical and in biological science and in sociology, the theory of probability and the curves of error are now of great importance. It is impossible to predict the life of an individual man, or the velocity of a particular molecule at any future instant ; but, with a sufficient number of molecules or men, we can deal with them statistically, and predict within narrow limits how many of them will be moving within a certain range of velocity or how many will die in a given year—philosophically we may say that we reach a form of statistical determinism, though, at this stage, individual uncertainty remains." *

In the next chapter we shall consider the application of statistical methods to the distribution of molecular velocities, and we shall meet with other illustrations of these methods when dealing with quantum mechanics.

* Dampier-Whetham, *A History of Science*, p. 251, C.U.P. (1930).

QUESTIONS

CHAPTER XLI

1. Give a mathematical definition of *probability*, and show that if three unlike coins are tossed the probability of any assigned complexion occurring will be 1/8.

2. What is meant by the *modulus of precision*? Draw graphs to illustrate the probability curves when the measurements made are (*a*) very accurate, and (*b*) contain widely divergent results.

3. Write a short account of the theory of errors, pointing out how the Gaussian Law may be applied to various widely differing phenomena.

4. If two dice are thrown, show that the probability of the sum of the numbers being five is 4/36.

5. Assuming that the most probable value of a number of observations is such that the sum of the squares of the residuals (errors) is the least, prove that the arithmetical mean has the greatest probability.

MAXWELL'S DISTRIBUTION LAW

WE shall now consider the use of statistical methods in the kinetic theory of gases, and examine the important law first put forward by Maxwell, known as the law of distribution of molecular velocities. It was pointed out in the last chapter that the normal law of errors can be relied upon to give satisfactory results only when large numbers are involved. The enormous number of atoms or molecules constituting a minute fragment of matter has been repeatedly emphasised. It is only within recent times that it has been possible to experiment on *individual* atoms or electrons. In theoretical physics it is often necessary to employ **statistical methods** to deal with the problem of large numbers of individuals, but the methods are those which must be applied on the macroscopic scale to the objects of our sense perceptions. One important problem of statistics is to determine how the individuals composing a given assembly are distributed among different possible states. Thus the actuary may consider how the population of a given country is distributed according to the annual income of the individuals. In this case he would graduate the income in finite intervals in some assigned way. The object may be to determine the **statistical probability** of the distribution of states in question. In like manner the physicist may set himself the problem of determining how the kinetic energy is distributed among the molecules composing a given amount of gas at some definite temperature.

Development of the kinetic theory of gases. In the seventeenth century several philosophers developed in a qualitative fashion an atomic theory of matter, and on this basis Gassendi was able to explain the existence of three states of matter and the possibility of transitions from one state to another, in a way little different from that of the modern kinetic theory. Boyle, and in particular Hooke, employed similar ideas as to the structure of matter and applied them to gases. Daniel Bernoulli, in his *Hydrodynamica*, 1738, deduced Boyle's law and tried to obtain a general relation between pressure and volume. taking into account the finite size of the molecules. Waterston (1845) was the first to attempt a scientific mathematical theory of the subject, and he enunciated the equipartition

of energy.   Clausius (1857) found the relation between temperature, pressure and volume for a gas.   Clerk Maxwell's first paper on molecular velocities was read at Aberdeen in 1859.   Boltzmann did important work in confirming and extending Maxwell's theory.

In his commemorative address delivered in 1931 at the Maxwell centenary, Max Planck said :

" To the simple relations connecting the mean velocity of the molecules with the pressure and specific heat, which had been derived by his predecessors, Maxwell added a new and more fundamental set of considerations, by enquiring as to the actual velocity of any molecule selected at random.   By his answer to this question Maxwell laid the foundations of a new branch of physics, that of statistical mechanics.   For it is clear that the question can only be answered by a probability law, that is, by a law which gives the fraction of the molecules which are found to possess a definite velocity when the experiment of selecting a molecule at random is repeated a great number of times.   This law, first found by Maxwell and named after him, was seen to be identical with the Gaussian Error Law, so long at any rate as the three components of the velocity vectors could be considered as independent."

An incident bearing on his work on the distribution law is thus recorded in the *Life of James Clerk Maxwell*.   " On one occasion he was wedged in a crowd attempting to escape from the lecture theatre of the Royal Institution, when he was perceived by Faraday, who, alluding to Maxwell's work among the molecules, accosted him in this wise—' Ho, Maxwell, cannot you get out ?   If any man can find his way through a crowd it should be you.' "

Ludwig Boltzmann recognised at once the fundamental position of Maxwell's velocity distribution law in the kinetic theory of gases.   Planck writes :

" Boltzmann first refined and generalised Maxwell's proof, which assumed monatomic spherical molecules, to cover the case of polyatomic molecules.   He showed further, by means of his well-known H-theorem that not only does the Maxwell distribution remain stationary, once it is attained, but that it is the only possible equilibrium state, since any system will eventually attain it, whatever its initial state.

" Boltzmann showed further that with every degree of freedom of a molecule of a gas in a steady state is associated the same average energy."

MAXWELL'S DISTRIBUTION LAW

The most important problem in the kinetic theory of gases is to determine the law of distribution of velocities, that is, the law according to which

the velocities of the molecules of the gas are grouped about the mean value. Maxwell's paper on the subject, communicated to the British Association at Aberdeen in 1859, was published in the *Philosophical Magazine* in 1860.

In discussing the distribution law we shall begin by merely stating the result of the investigations, leaving the formal proof till later. We assume that the gas is devoid of mass motion, so that there is no streaming of the gas as a whole in any particular direction. Maxwell's own proof is admitted to be unsatisfactory, because it *assumes* the three velocity components to be independent. For each component Maxwell's result may be stated as follows :

If N is the total number of molecules in an enclosure (this number being assumed invariable) and u, v, w are the velocity components of a typical molecule, then the number of molecules having a velocity component between u and $u + du$ is

$$N \sqrt{\frac{m}{2\pi kT}} \, e^{-\frac{mu^2}{2kT}} \, du,$$

with similar expressions applicable to the components parallel to the axes y and z. Each of the three expressions is of the form $y = e^{-x^2}$ which represents the law of errors of Gauss (Fig. 286).

The value of a selected velocity component is plotted as abscissa on the x-axis and the *area* of a narrow strip between x and $x + dx$ determines the number of molecules concerned. The total number of molecules is given by the whole area under the curve.

It should be noticed that for a given enclosure, containing a particular gas, there are only two physical quantities at our disposal :

FIG. 286.   GRAPH OF THE FUNCTION $y = e^{-x^2}$ FOR POSITIVE VALUES OF x

(1) the total number of molecules, N. This number determines the *density* of the gas.

(2) The total energy of the molecules, E.

Since (p. 321) $E = N\overline{w} = N\alpha T = \tfrac{3}{2}NkT,$

the total energy determines the *temperature* of the gas when N is known.

In deriving the law of distribution certain assumptions are made which require attention.

1. We assume that a gas in an enclosure maintained at a constant temperature assumes a steady state in which it is in thermal equilibrium with its surroundings.

2. In the steady state we assume that the density of the gas remains uniform on the average throughout the gas, and throughout the time under consideration.

3. We further assume that the velocities of the molecules are distributed according to some law. This does not mean that the velocities are fixed, but that the number having velocities between prescribed limits does not depend on the position of the selected " cells " * or on the time at which the examination is made.

Let u, v, w be the component velocities of a molecule.

Let N be the total number of molecules.

In the steady state the number of molecules having a velocity with components between u and $u + du$, v and $v + dv$, w and $w + dw$ is

$$dn = Nf(u, v, w)\, du\, dv\, dw.$$

The object of the investigation is to find the form of the function f.
It was found by Maxwell that this function has the form

$$f(u, v, w) = Ae^{-hm(u^2 + v^2 + w^2)}$$

where A and h are constants.

Assuming this result, we may write

$$dn = NAe^{-hm(u^2 + v^2 + w^2)}\, du\, dv\, dw,$$

or $\qquad dn = NAe^{-hmu^2}\, du \,.\, e^{-hmv^2}\, dv \,.\, e^{-hmw^2}\, dw$

(We notice that three factors of the form $e^{-hmu^2}\, du$ are multiplied together, a result which might have been anticipated *on the assumption* that the velocity components may be treated independently as was done in Maxwell's first investigation. Such an assumption, however, requires justification.)

The value of the constant A may be found by expressing the fact that the *total* number of molecules is N, that is,

$$\int dn = N.$$

This gives for A the value

$$A = \left(\frac{hm}{\pi}\right)^{\frac{3}{2}}.$$

The quantity h (which must not be confused with Planck's constant)

* The technical meaning of this term is explained later in the chapter.

may be expressed in terms of the mean square velocity C^2, or in terms of the mean molecular energy $\mathbf{w}$.   It can be shown that

$$\mathbf{w} = \tfrac{1}{2}mC^2 = \frac{3}{4h}.$$

Thus it is found that $h = \dfrac{3}{4\mathbf{w}}.$

But $\mathbf{w} = \tfrac{3}{2}kT,$ so that $h = \dfrac{}{2kT}.$

For a gas devoid of mass motion the number of molecules having a velocity with components between u and $u+du$, v and $v+dv$, w and $w+dw$, is

$$N\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} e^{-hm(u^2+v^2+w^2)}\, du\, dv\, dw.$$

Substituting the value of h stated above, this gives

$$N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m(u^2+v^2+w^2)}{2kT}}\, du\, dv\, dw.$$

Further, it is found that the number of molecules having a resultant velocity between c and $c+dc$, without any reference to the direction of this resultant, is

$$dn_c = 4\pi N\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} e^{-hmc^2}c^2\, dc = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}}c^2\, dc.$$

The presence of the factor c^2 in this last expression should be noticed. The curve representing this function, $y = 2x^2 e^{-x^2}$, is shown in Fig. 287,
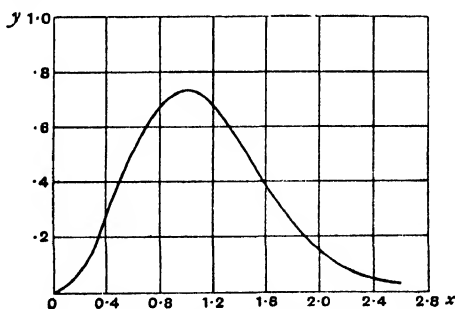
FIG. 287.   GRAPH OF THE FUNCTION $y = 2x^2 e^{-x^2}$

the diagram having been drawn to the same scale as Fig. 286.   The factor 2 has been introduced into the equation of the second curve so that the two curves may have the same area, namely $\tfrac{1}{2}\sqrt{\pi}$.

We must distinguish between the **root mean square velocity C** and the **mean velocity** $\bar{c}$.

C^2 is the arithmetical mean of the values of c^2:

$$C^2 = \bar{c^2} = \frac{1}{N} \int_0^\infty c^2 \, dn_c = \frac{3}{2hm}.$$

Here we have replaced the ordinary sum, Σc^2, by an integral.

(The element of volume concerned is supposed to be large enough to hold an immense number of molecules. Since there are about $2 \cdot 9 \times 10^{16}$ molecules in a cubic millimetre of gas under normal conditions, this replacement of a sum by an integral is legitimate.)

The *mean* velocity $\quad v = \bar{c} = \dfrac{1}{N} \int_0^\infty c \, dn_c = \dfrac{2}{\sqrt{\pi h m}}.$

The *most probable* velocity, c_0, is that which gives a maximum value for dn_c. It is given by

$$c_0 = \frac{1}{\sqrt{hm}}.$$

Hence $\qquad \dfrac{v}{C} = \sqrt{\dfrac{8}{3\pi}}.$ The average velocity is *less* than the root mean square velocity.

$$\frac{c_0}{C} = \sqrt{\frac{2}{3}}.$$

$\dfrac{v}{c_0} = \dfrac{2}{\sqrt{\pi}}.$ The average velocity is *greater* than the most probable velocity.

If N is the *total* number of molecules in an enclosure, the number having a velocity component between u and $u + du$ is, as has already been stated,

$$N \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mu^2}{2kT}} du.$$

The number N' which cross an element of surface of area 1 sq. cm. in unit time in a given direction, or which strike 1 sq. cm. of the wall in unit time, is

$$N' = \int_0^\infty u \, dn = \frac{N}{2\sqrt{\pi h m}} = \frac{Nv}{4} = \frac{NC}{\sqrt{6\pi}}.$$

This result has several important applications, and accordingly deserves special mention.

EXPERIMENTAL EVIDENCE FOR MAXWELL'S DISTRIBUTION LAW

For a long period evidence in favour of Maxwell's distribution law for gaseous molecules was necessarily of an indirect nature. We know that " transport " phenomena in gases are not associated with equilibrium conditions, and involve a consideration of the mean free path of the molecules. Most of the phenomena studied (viscosity, diffusion, and

thermal conductivity) were not such as to justify the application of the hypothesis of a steady state and consequently could not be treated rigorously by the method of mean free paths.* In fact as soon as the temperature of a gas is no longer uniform, the molecular velocities cease to be distributed according to Maxwell's law. The law also fails as soon as the pressure is no longer uniform.

By assuming a particular law of intermolecular action, namely that of the inverse fifth power of the distance, Maxwell was able to calculate the transport of momentum, matter and energy by the molecules of a gas, as exhibited in the phenomena of gaseous viscosity, diffusion and thermal conductivity. The theory has since been extended by other investigators. By considering the **mean free path,** that is, the mean distance that a molecule travels between collisions, it is possible to deduce approximate results as to the value of a physical property of a gas, say the viscosity, as we have already seen from the theory of transport phenomena in Chapter XXVIII. But our knowledge of the laws of collisions between molecules is not sufficient to permit of our giving an *accurate* prediction. Knudsen † has shown how to overcome this difficulty by making the dimensions of the apparatus small compared with the mean free path at the pressures used.

Method of molecular rays. This method has been developed in the Hamburg Institute for Physical Chemistry under the direction of Professor Otto Stern, who writes : " The method was used initially to verify the fundamental postulates of the gas kinetic theory. Naturally there was never any doubt about their validity ; but it was none the less satisfactory that one was able to demonstrate so absolutely directly the linear motion of the molecules, to measure their velocity, and so forth."

The method and technique of the experiments have been described by R. G. J. Fraser in his book *Molecular Rays* (Cambridge, 1931). Suppose
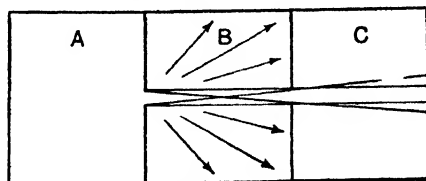
FIG. 288. THE METHOD OF MOLECULAR RAYS

a small aperture is made in the wall of a vessel *A* containing a gas, so as to allow molecules to pass through it into an evacuated space *B* (Fig. 288).

* Eugène Bloch, *The Kinetic Theory of Gases*, Chapter III (1924).

† Knudsen, *The Kinetic Theory of Gases : Some Modern Aspects* (Methuen, 1934).

The molecules in *B* will traverse rectilinear paths radiating out from the aperture.   By making a second aperture in a suitable position in the wall of *B* some of these molecules will pass into a third chamber *C* where they may be detected when they impinge on the wall.   The molecules in *C* for all practical purposes do not encounter one another, and form a geometrically defined beam or **molecular ray.**   Dunoyer in 1911 verified these deductions from gas theory, using sodium vapour (which is monatomic) and observing the " umbra " and " penumbra " formed on the glass wall of chamber *C*.

A molecular ray may be defined as a beam of *neutral* molecules, moving *in vacuo* with thermal velocities corresponding to the temperature of the source.   The *ray* is practically collision free, whereas a *jet* of gas is in turbulent motion and cannot maintain its form.

Two problems of technique arise : (1) the production of a molecular ray of sufficient intensity, and (2) the detection of the ray by suitable means adapted to the molecular species concerned.   The fundamental principles involved in the production of intense molecular beams of narrow cross-section were laid down in 1926 by Stern.

The first attempt to make a direct determination of molecular velocities was that of Stern six years earlier (1920).   He used atoms of silver obtained by heating a silvered platinum wire to the melting point of silver by the passage of an electric current.   The wire was stretched along the axis of two coaxial vertical cylinders (Fig. 289).   The inner cylinder contained a slit *S* through which a stream of silver atoms emerged.   The whole apparatus was evacuated and could be set in rotation at a high speed about the axis.

When the apparatus is at rest the stream of atoms impinges on the outer cylinder at *A* (Fig. 289).
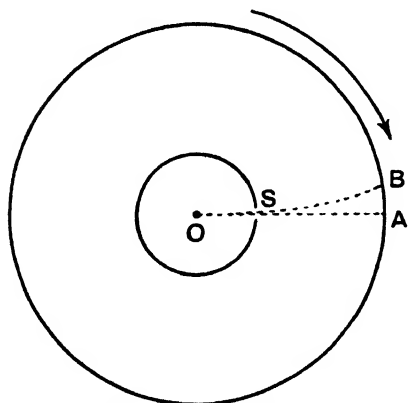
FIG. 289.   EXPERIMENT OF STERN

When the rotation is clockwise the stream condenses at a point such as *B*.

The more rapidly moving atoms will condense nearer *A* than the slower atoms, so that a **velocity spectrum** will be found.   The apparatus was rotated first in the clockwise and then in the anticlockwise direction, so that two deflected traces were obtained.   These were rather broad and diffuse in outline in consequence of the statistical distribution of velocities.

The average velocity calculated from the middle of the deflected trace was about 660 metres per second, corresponding approximately with the velocity calculated from the known temperature.

In 1927 J. A. Eldridge * subjected Maxwell's theory to a direct experimental test.   The apparatus was designed to give a velocity spectrum for a metallic vapour, cadmium being used in the actual experiments. The vapour passed through a slit about 0·1 mm. wide in the wall of the furnace into a highly evacuated tube.   In this tube were a number of coaxial disks with radial slots rotating at high speed.   These were driven by an induction motor.   The beam of atoms after passing through the slots was condensed on a cooled glass plate.   The rotating slits acted as a " velocity filter " so that the atoms fell on the plate at a point depending on their velocity.   The density of the deposit on the plate at different points was measured photometrically, and was found to agree well with Maxwell's distribution law of molecular velocities.

The method bears an analogy to Fizeau's method of measuring the velocity of light by means of a rotating toothed wheel.   In Fizeau's experiment the light is reflected back towards the original wheel, whereas in dealing with the cadmium atoms a series of wheels is mounted on a common axis.

In 1929 Lammert, working in Stern's laboratory, constructed an apparatus for the production of rays of mercury atoms travelling with uniform velocity.   The method avoided some of the difficulties involved in the earlier experiments. and by comparing the intensities of selected velocity ranges against the total beam intensity gave reliable and direct verification of the Maxwell distribution law.

THEORETICAL DISCUSSION OF MAXWELL'S LAW †

Complexions of a molecular system.   Consider a system composed of a very large number (N) of ideal molecules.   Each molecule is supposed to possess minute mass and extension (it may be regarded as a **mass-point**). The **configuration** of the system can only be defined precisely by assigning definite coordinates to each particle.   We regard a **complexion** of the molecules as defined by assigning a **range of configuration.**   Instead of saying that a molecule is at a *definite point* (x, y, z), we say that its coordinates lie between x and $x + \delta x$, y and $y + \delta y$, z and $z + \delta z$, where δx, δy, δz are small but *finite* quantities.   We divide the whole volume into a *finite* number of **cells**, the volume of a particular cell being $\delta x \, \delta y \, \delta z$. The presence of a molecule in an assigned cell is analogous to a coin or a die showing a certain **aspect** after tossing.

A **complexion** of the system is defined by the aspects of the molecules,

---

that is, by the way they are distributed among the cells. Assuming N molecules and c cells, the **number of complexions** in which

n_1 molecules are in cell 1
n_2 ,, ,, 2
n_r ,, ,, r
n_c ,, ,, c

is

$$\frac{N!}{n_1! \, n_2! \, n_3! \, ... \, n_c!} = P \text{ (say).}$$

P is called the **complexion number** or the **possibility number**.
When n is a large number it follows from Stirling's theorem that

$$\log n! \simeq n \log n - n.$$

Hence, provided none of the numbers n_r is too small,

$$\log P \simeq N \log N - \overset{r=c}{\underset{r=1}{\Sigma}} n_r \log n_r.$$

By assigning a maximum value to P, subject to the condition that $n_1 + n_2 + ... + n_c = N$, it is possible to deduce information as to the distribution of the molecules in space when the steady state is established. In this way we arrive at the somewhat trite conclusion that a uniform distribution is more probable than any other, or the density of the gas is on the average the same at all points. For a discussion of this case, which illustrates the *method* employed in later work, the reader is referred to Max Born's *Atomic Physics*, Chapter I.

In considering a molecular system in greater detail we must take into account the *motions* of the molecules as well as their *positions*. The velocity components of a particular molecule at (x, y, z) may be represented by (u, v, w). The six components x, y, z, u, v, w determine a **phase** of that molecule. An **aspect** of the molecule is determined by saying that the first coordinate lies between x and $x + \delta x$, etc. ; the first velocity component between u and $u + \delta u$, etc. We call the magnitude $\delta x \, \delta y \, \delta z \, \delta u \, \delta v \, \delta w$ an element of **extension in phase**, or a **phase cell**. This geometric term is borrowed from the previous case and to it is attached an analogous idea. The six components typified by x, y, z, u, v, w may be regarded as determining the position of a " representative point " in a 6-dimensional space. Although we may be employing terms applicable to space of 6 dimensions, there is no need to attempt to visualise such a many-dimensional space. The *algebraic* work is exactly similar to that already employed in three dimensions.

Instead of specifying the velocities of the particles it is sometimes convenient to specify the momenta. The components of the momentum of a particular particle are $p_x = mu$, $p_y = mv$, $p_z = mw$. The **microscopic state** of the particle is then determined by six coordinates, the three positional coordinates x, y, z and the three momenta coordinates p_x, p_y, p_z. These six coordinates determine a **representative point**. The element of hyper-space is now $\delta x \, \delta p_x \, \delta y \, \delta p_y \, \delta z \, \delta p_z$. In passing, it may be noted

that the product $\delta x \, \delta p_x$ has the dimensions of "action", and later, when considering the quantum theory, it will be convenient to equate the product to Planck's constant h, the element of hyper-space on this view being equal to h^3.

In considering the **probability of a complexion** a fundamental *postulate* is introduced. If the various phase cells have the same magnitude, *one aspect of a given molecule is as probable as any other*. In other words, it is just as likely for the "representative point" in the "phase diagram" to be in any "phase cell" as in any other.

The possibility number for the distribution of the molecules in the phase cells is (as in the simpler case already described)

$$P = \frac{N!}{n_1! \, n_2! \, \dots \, n_r! \, \dots \, n_c!} = \frac{N!}{\Pi n_r!},$$

and the mathematical probability is

$$W = \frac{P}{c^N}.$$

Limitations on the total number of possible complexions. There are two *limitations* which must be taken into account in considering the number of complexions. In the first place the *total number* of molecules is limited, being equal to N, say. This means that

$$n_1 + n_2 + n_3 + \dots + n_r + \dots + n_c = N.$$

So far we have not introduced any dynamical property. We know that, at constant temperature, the total *energy content* is fixed, being equal to some value E, say.

That is, $n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_r \epsilon_r + \dots + n_c \epsilon_c = E$,

where ϵ_1, ϵ_2, ϵ_3, $\dots \epsilon_r \dots \epsilon_c$ are the energies of a molecule in cell $1, 2, 3, \dots r \dots c$, respectively, and E is the total energy. For an ideal gas ϵ_r is of the form $\frac{1}{2}m(u^2 + v^2 + w^2)$.

State of maximum probability. The next step is to determine the state of thermodynamic equilibrium which we assume to be the state corresponding to maximum probability. In finding this state we must bear in mind the two limitations just described.

The problem is now to determine the maximum value of the possibility number

$$P = \frac{N!}{\Pi n_r!},$$

subject to the limitations $N = \Sigma n_r$

and $E = \Sigma n_r \epsilon_r.$

It is convenient to introduce a new quantity defined by $\omega_r = n_r/N$. Since this is the ratio of the number of molecules in the rth cell to the *total* number of molecules it is called the **partition function**. Obviously

$$\Sigma \omega_r = 1, \quad \text{and} \quad n_r = N\omega_r.$$

We use Stirling's theorem to obtain a simple expression for $\log_e P$, and find without difficulty

$$\begin{aligned}
\log P &= N(\log N - 1) - \Sigma n_r(\log n_r - 1) \\
&= N(\log N - 1) - \Sigma N\omega_r(\log N + \log \omega_r - 1) \\
&= N(\log N - 1) - N\Sigma\omega_r(\log N - 1) - N\Sigma\omega_r\log \omega_r \\
&= -N\Sigma\omega_r\log \omega_r.
\end{aligned}$$

Thus we have three equations,

$$\left.\begin{aligned}
\log P &= -N\Sigma\omega_r\log \omega_r \\
N &= \Sigma n_r = N\Sigma\omega_r \\
E &= \Sigma n_r\epsilon_r = N\Sigma\epsilon_r\omega_r
\end{aligned}\right\},$$

and the condition for maximum probability is

$$\left.\begin{aligned}
\delta \log P &= -N\Sigma(1 + \log \omega_r)\delta\omega_r = 0 \\
\delta N &= N\Sigma\delta\omega_r = 0 \\
\delta E &= N\Sigma\epsilon_r\delta\omega_r = 0
\end{aligned}\right\}.$$

By using undetermined multipliers (Lagrange's method),

$$\Sigma(\log \omega_r + \lambda + \beta\epsilon_r)\delta\omega_r = 0,$$

where λ and β are the multipliers employed.

Since the variations are (now) quite arbitrary,

$$\log \omega_r + \lambda + \beta\epsilon_r = 0,$$

which leads at once to $$\omega_r = \frac{1}{f}e^{-\beta\epsilon r},$$

where f is a constant.

This result determines the value of the partition function ω_r, which gives the proportion of atoms having the energy ϵ_r.

The quantity β may be called the **distribution constant** * of the system. It is *inversely* proportional to E/N, the average energy of a molecule, and by using Boltzmann's hypothesis connecting probability and entropy it can be shown that $\beta = 1/kT$, where k is Boltzmann's constant.

Thus we see that, for the state of maximum probability, ω_r is proportional to $e^{-\epsilon_r/kT}$, which is equivalent to the Maxwell-Boltzmann law of distribution.

The significance of the constant f may be seen as follows. Since

$$f\omega_r = e^{-\epsilon_r/kT}, \quad f\Sigma\omega_r = \Sigma e^{-\epsilon_r/kT}.$$

But $\Sigma\omega_r = 1$,   so that $f = \Sigma e^{-\epsilon_r/kT}.$

Thus f represents the **sum of the partition functions** (in German, " Zustandsumme ").

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* Rice in *Introduction to Statistical Mechanics* (1930) uses the symbol μ for the distribution constant.

QUESTIONS

CHAPTER XLII

1. State Maxwell's law of distribution of velocities, and specify the conditions required for the validity of the law.

Describe any important experimental investigation of the law of distribution of velocities.   (St. A. U).

2. Assuming Maxwell's law of distribution of velocities in a gas, find an expression for the number of molecules which cross any surface per unit area per second, and hence show that the mass of gas striking any surface per unit area per second on one side is given by $\rho\sqrt{\dfrac{\bar{R}T}{2\pi m}}$ in a standard notation.   (St. A. U.)

3. State and explain Maxwell's expression for the distribution of velocities among the molecules of a gas.

Show how to deduce an expression for the number of molecules crossing unit area of one of the coordinate planes, and for the average kinetic energy parallel to one of the coordinate axes.   (St. A. U.)

4. Write a short account of the method of molecular rays, indicating how the rays are produced and detected.

5. Explain how molecular velocities have been determined by the method of molecular rays, and state the results obtained.

ENTROPY AND PROBABILITY

BEFORE taking up the subject of the newer quantum statistics it is desirable to consider further a question which has already been mentioned in Chapter XXXIX on the quantum theory of radiation, namely the relation between entropy and probability. In this connection the " heat theorem " of Nernst also merits further consideration.

The philosophical aspects of these problems have received much attention, having been discussed at length by many writers. Here it is necessary to refer briefly only to some of the more outstanding points of physical interest.

ENTROPY AND PROBABILITY

In thermodynamic theory a certain function of the state of a substance is introduced which is called **entropy,** and is defined as follows. When a substance undergoes a reversible change, and in so doing takes in a quantity of heat δQ at absolute temperature T, its entropy is said to increase by an amount $\delta Q/T$. It will be noticed that this statement defines only the *change δS* in the entropy, the absolute value being left undetermined. The importance of this function arises from the fact that the change in entropy does not depend on the particular reversible process by which the substance is brought from one state to another.

In 1849 Rankine communicated to the Royal Society of Edinburgh a paper based on the " Hypothesis of Molecular Vortices ". The quantity of heat in a body is the energy of these vortices ; the absolute temperature is the same energy divided by a specific coefficient for each particular substance. Rankine used in symbols a quantity corresponding to entropy and afterwards suggested for it the name " Heat-Potential " or " Thermo-dynamic Function ", a name adopted by some writers.

Clausius in 1854 investigated the properties of a function which he called " Aequivalenzwerth " and later " Entropie " which is closely related to the Thermodynamic Function of Rankine. According to Clausius *the entropy of the universe tends to become a maximum.* This is another way of regarding Thomson's doctrine of the dissipation of

energy, according to which the " available energy " of the universe is tending towards zero.   Referring to this doctrine Helmholtz wrote .

" These consequences of the Law of Carnot are, of course, only valid provided that the law, when sufficiently tested, proves to be universally correct.   In the meantime there is little prospect of the law being proved incorrect.   At all events, we must admire the sagacity of Thomson, who, in the letters of a long-known little mathematical formula, which only speaks of the heat, volume, and pressure of bodies, was able to discern consequences which threatened the universe, though certainly after an infinite period of time, with eternal death."

It was Willard Gibbs who first suggested a relationship between entropy and probability :   " The impossibility of an uncompensated decrease of entropy seems to be reduced to improbability."   Boltzmann (1877) developed the idea that increase in entropy corresponds to an increase in the degree of disorganisation of the coordinates describing the positions and motions of the molecules composing the substance or system.

Logically the absolute scale of temperature is derived from the second law of thermodynamics.   This law may be expressed in terms of entropy by saying that every process in nature takes place in such a way that the sum of the entropies of all bodies taking part in the process increases. In the limiting case of a reversible process the sum remains constant. This is the most general way of stating the second law.   It is not surprising then that the study of entropy should be so important in relation to statistical mechanics, and in fact it was shown by Boltzmann that it was possible to give a statistical interpretation of entropy.   The temperature of a gas is a measure of the average energy of the molecules.   The heat energy of a gas is the energy of the random motion of the molecules. If we wish to obtain mechanical energy from the gas it is necessary that the molecules, or a majority of them, should move in ordered fashion in some assigned direction, as when they drive a piston along a cylinder. That is to say, chaotic motion must be converted into ordered motion. This is clearly a more difficult process than the conversion of orderly motion into disorderly motion.

To illustrate the difference between an ordered and a disordered state we may employ the following instructive example.   Let us construct a box divided into two compartments which are open to each other, and let us place a number of red balls in one compartment and a number of black balls in the other.   This represents an ordered arrangement of the balls.   By shaking the box for a considerable period, a number of red balls will pass into the second compartment and a number of black balls into the first.   We shall obtain a disordered state corresponding

to what may be termed a chaotic distribution. It would be very difficult, if not impossible, to reverse the process and merely by shaking to get the balls once more into an orderly state. Even if we could see the individual balls the manipulation necessary would be extremely difficult, and when we know nothing of the individuals until the box is opened there is little likelihood of finding all the red balls collected in one compartment and all the black in another. The disordered states are more probable than the ordered states.

The relation between the molecular order of a substance and its entropy has been employed practically in the paramagnetic method of obtaining very low temperatures as described in Chapter XXXIV.

The " random element " in physics. In Chapter IV of his book on *The Nature of the Physical World*, Eddington discusses with delightful humour " The Running-down of the Universe ". He begins by considering the process of shuffling a pack of cards, and points out that there is only a ghost of a chance that a thoroughly shuffled pack will some day be found in the original order. He then puts forward the contention that

" Whenever anything happens which cannot be undone, it is always reducible to the introduction of a random element analogous to that introduced by shuffling."

" The practical measure of the random element which can increase in the universe but can never decrease is called *entropy*." " Time's arrow " points in the direction of increase of the random element. . . . " So far as physics is concerned time's arrow is a property of entropy alone." *

The entropy of a system may be regarded as a measure of what Willard Gibbs called the " mixed-upness " of the system, corresponding to the conception which was developed in mathematical form by Boltzmann (1877). The problem has been stated very clearly by Sir Oliver Lodge in his book *Beyond Physics*.

When heat passes from a hot body to a cold the entropy of the system is in general greater than before. For instance, the process of thermal conduction is automatic and uncontrolled, and in the transfer of a given amount of heat the cold body gains more entropy than the hot body loses.

When, however, the operation is under human control, as in the working of an ideal heat engine, there need be no increase of entropy. " Heat is taken from a hot body at one temperature, part of it is converted into the energy of mechanical movement, say of pistons and flywheel, and only the balance is given to a body at low temperature." In such a case the total entropy may remain constant.

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* In *Philosophy and the Physicists* Stebbing has taken objection to the view that entropy may be regarded as " the signpost of time ". The experimenter must be aware of the order of his observations before he can draw conclusions from them.

As we have seen in an earlier chapter, it is when the operation is carried out in a reversible manner that the entropy remains unchanged. Every irreversible operation implies the increase of entropy. "Once an irreversible operation has been performed, there is no remedy, it cannot be undone. Time has gone on, and it cannot go backwards. Entropy has been irremediably increased."

The second law of thermodynamics may be stated in the form : In all physical and chemical processes occurring in nature the entropy of a system of bodies tends to increase. In the limiting case of a reversible process the entropy remains constant.

Another aspect of the question has been emphasised by G. N. Lewis,* who holds that increase of entropy "corresponds merely to a loss of information with regard to a state of a system and is thus a purely subjective concept." For Maxwell's "demon" (p. 629) it would be possible to carry out a sorting process and separate rapidly moving from slowly moving molecules.

It has been suggested that the second law of thermodynamics as expressed in terms of increase of entropy, implies the final extinction of all activity in the universe.

The question of the "heat death" of the universe has been discussed in an interesting way by R. A. Millikan.† He argues that it is not legitimate to make a sweeping generalisation from man's experience on the surface of the earth to the universe in all its parts. His conclusion is in agreement with the dictum of G. N. Lewis : "Thermodynamics gives no support to the assumption that the universe is running down. Gain in entropy means loss of information and nothing more."

Boltzmann's relation between entropy and probability. Boltzmann came to the conclusion that "the entropy of a physical system in a definite state depends solely on the probability of that state", in other words, there is a functional relationship between entropy and the "probability" of the state.

According to his treatment, the way in which entropy depends on probability may be determined by an argument of a very general character.

Let S be the entropy, W the maximum probability of a physical system in a definite state, then the former is some function of the latter or

$$S = f(W).$$

"In whatever way W be defined, it can be safely inferred from the mathematical concept of probability that the probability of a system

* *Science*, Vol. 71, p. 569 (1930) ; Lewis and Randall, *Thermodynamics* (1923), Chapter XI.

† *Electrons*, pp. 454-5 (1935).

which consists of two entirely independent systems is equal to the product of the probabilities of these two systems separately."

That is $$W = W_1 W_2.$$

If S_1 and S_2 are the entropies of the systems in the two states,

$$S_1 = f(W_1), \quad \text{and} \quad S_2 = f(W_2).$$

But $$S = S_1 + S_2.$$

Hence $$f(W_1 W_2) = f(W_1) + f(W_2).$$

From this **functional equation** the form of the function f can be determined.

Differentiate both sides with respect to W_1, W_2 remaining constant.

$$W_2 \dot{f}(W_1 W_2) = \dot{f}(W_1),$$

where the dot over the function f indicates differentiation with respect to W and $\dot{f}$ represents $\partial F/\partial W$.

Differentiate with respect to W_2, W_1 remaining constant.

$$\dot{f}(W_1 W_2) + W_1 W_2 \ddot{f}(W_1 W_2) = 0,$$

or $$\dot{f}(W) + W\ddot{f}(W) = 0.$$

This is a differential equation of the second order, and it can be shown* that the general integral of the equation is

$$f(W) = k \log_e W + \text{a constant}.$$

In this expression the constant of integration k, now named after Boltzmann, is to be regarded as a *universal* constant, that is to say, it will have the same value for any system that may be chosen, no matter whether one chooses a terrestrial or a cosmic system. When once the value of k has been found for any assigned system, the same value may be employed for any other system. The accurate determination of Boltzmann's constant accordingly represents one of the important problems of physical measurement.

Boltzmann's theorem as to entropy can be written

$$S - S_0 = k \log_e (W/W_0),$$

where $S - S_0$ is the difference in entropy in two particular states and W, W_0 are the maximum probabilities of the two states under considera-

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* The differential equation is of the typical form $\frac{dy}{dx} + x\frac{d^2y}{dx^2} = 0$. Writing p for $\frac{dy}{dx}$, this becomes $p + x\frac{dp}{dx} = 0$, or $p = -x\frac{dp}{dx}$. Thus $\frac{dp}{p} = -\frac{dx}{x}$, which yields on integration $\log p = -\log x + \text{constant}$. Therefore $\log(px)$ is constant, and obviously px is constant. This result may be written $x\frac{dy}{dx} = k$ (a constant), so that $dy = k\frac{dx}{x}$, which on integration gives $y = k \log x + \text{constant}$.

tion. It is assumed that this maximum probability can be calculated from a statistical treatment of the motion of the molecules.

Determination of Boltzmann's constant k. Assuming the above expression of Boltzmann's law, it is not difficult to show that k in the equation is the same as the gas constant (R/N) for a single molecule.

For consider N molecules of a perfect gas confined in a volume V as contrasted with the same number of molecules in a larger volume V_0. The comparative probability of a single molecule finding itself in the smaller volume V instead of in the larger volume V_0 is clearly V/V_0. The same is true for a second molecule, and the comparative probability for both molecules is $(V/V_0)^2$. Proceeding in the same way for all the molecules, the comparative probability is $(V/V_0)^N$. This means that

$$\frac{W}{W_0} = \left(\frac{V}{V_0}\right)^N.$$

Boltzmann's law yields $\quad S - S_0 = kN(\log V - \log V_0)$.

Using the second thermodynamic relation of Maxwell (p. 652),

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_T,$$

we find

$$\frac{p}{T} = \frac{kN}{V}.$$

But this is simply the familiar gas law $pV = kNT$, showing that $kN = R$, or $k = R/N$.

Thus k is identical with the gas constant reckoned for a single molecule of an ideal monatomic gas (Chapter XIV, p. 321).

The numerical value of k is $(1.3708_9 + 0.0014) \times 10^{-16}$ erg $\times$ deg.$^{-1}$ (Birge, 1929).

Criticisms of Boltzmann's method. Close examination of the foregoing argument which connects together entropy and probability reveals certain weaknesses. In particular no definite method of estimating probability is indicated. R. H. Fowler,[*] in particular, has given a searching criticism of the method originated by Boltzmann, and extended by Planck, of introducing entropy by relating it to probability, a method which Fowler claims to be " obscure or misleading and certainly unnecessary."

According to Fowler, Boltzmann's equation

$$S - S' = k \log W/W'$$

provides no basis for a logical definition of *absolute entropy*. " Much has been written of absolute entropy in the belief that in this way a basis could be found for Nernst's heat theorem. We shall show . . . that this theorem takes its natural place in the equilibrium theory of pure statistical

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[*] R. H Fowler, *Statistical Mechanics*, § 6·8, p. 137 (1929). See also p. 141.

mechanics, and can be formulated without reference to entropy at all, still less to absolute entropy." Although Planck assigned to entropy a quite definite absolute value, $S = k \log W,$

Fowler maintains that, " whatever the practical convenience of the idea of absolute entropy (often great), it is of no theoretical importance whatever ".

TWO STATISTICAL THEOREMS

The heat theorem of Nernst. The important theorem enunciated by Nernst in 1906 has already been discussed in Chapter XXXIV. For our present purpose it may be enunciated in the following form :

At the absolute zero of temperature all reactions in condensed systems take place without change in the value of the total entropy of the system ; or in symbols $\Delta S = 0, \quad \text{when} \quad T = 0.$

Let us think of a crystal of a pure substance at the absolute zero of temperature. Here we have no random distribution of molecules, and we may suppose that no random element remains, that is, when the positions and properties of a few molecules are fixed, the positions and properties of all other molecules are completely determined. According to Lewis and Gibson, this lack of any sort of random element is the theoretical basis for supposing that the entropy of a perfect crystal of a pure substance vanishes at the absolute zero. They conclude that " *every* substance has a finite *positive* entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances ".

Boltzmann's H-theorem. Statistical mechanics predicts that, in a system which has not already come into equilibrium, the changes taking place are in such a direction as corresponds to a more probable distribution. For example, in the case of a gas in which the molecules do not conform to the Maxwell-Boltzmann distribution law, there will be a readjustment of the configuration so as to approach this distribution. Boltzmann stated an important theorem, called the H-theorem, which gives an expression for the *rate* at which this approach takes place as a result of collisions between the molecules. The function H is defined by the equation

$$H = N_1 \log N_1 + N_2 \log N_2 + N_3 \log N_3 + \dots ,$$

where N_1, N_2, $N_3 \dots$ are the numbers of molecules in the different possible states assumed by the different kinds of molecules. Boltzmann then proceeds to investigate the probable value of $\dfrac{dH}{dt}$, which expresses the rate of change of H with the time. It is found that H is a quantity

which tends to decrease with the time and reach a minimum equilibrium value which is in agreement with the Maxwell-Boltzmann distribution law. The expression obtained for the decrease of H with time gives the *probable* rate of decrease, and does not rule out occasional increases.

There is an analogy between the increase in the thermodynamic quantity entropy and the decrease in the statistical mechanical quantity H. In fact, according to Boltzmann, we can write

$$S = -kH + \text{constant.}$$

On this view the sum $S + kH$ for an assigned system remains invariable.

QUESTIONS

CHAPTER XLIII

1. " The entropy of the universe is tending towards a maximum." Discuss this statement from the point of view of the Second Law of Thermodynamics.

2. Write a brief account of the " random element " in Physics.

3. Show in what way the entropy of a substance is related to its molecular order in that particular state. How has this conception been applied practically?

4. Discuss the relation between entropy (S) and maximum probability (W) of a system, and prove that $S = k \log W + \text{constant}$, where k is Boltzmann's constant.

5. Explain briefly the significance of the H-theorem of Boltzmann.

CHAPTER XLIV

STATISTICAL METHODS AND QUANTUM THEORY

Up to this point we have been considering statistical methods mainly in relation to classical mechanics. We now turn to the consideration of the modifications brought about through the introduction of the quantum theory. The theory has passed through two important stages, the first period extending over the first quarter of the twentieth century, and the second period dating from about 1926. The latter includes the later developments described as "quantum mechanics" or "wave mechanics", terms which must be regarded as essentially equivalent.

Simple harmonic oscillator. It will be convenient to begin our discussion by taking up a very simple dynamical problem which illustrates the principles and is easily visualised. This is the problem of the simple harmonic oscillator or resonator, which may be taken to represent the electric dipole of Hertz. The consideration of this dipole played an important part in the initiation of the quantum theory by Planck in 1900. The resonator may be thought of as composed of two poles charged with equal quantities of electricity of opposite sign, and only the motion in the direction of the fixed axis of the resonator will be considered. Thus the vibration of the resonator entails *one* degree of freedom only. This gives its special simplicity to the dynamical system. The motion of each particle is assumed to be of simple harmonic type, and the resonator is supposed to possess a definite *natural* frequency of vibration ν, or pulsatance ω where $\omega = 2\pi\nu$. If q is the **positional co-ordinate**, and p the **impulse co-ordinate** or momentum, $p = m\dot{q}$, m being an inertia coefficient. In the steady state of vibration, that is when the resonator is neither emitting nor absorbing energy, the equation of motion is

$$\dot{p} = -\mu q,$$

where μ is the restoring force per unit displacement.

Hence $$m\ddot{q} + \mu q = 0,$$

the differential equation typical of simple harmonic motion.

Putting ω^2 for μ/m, the equation becomes

$$\ddot{q} + \omega^2 q = 0,$$

the solution of which is known to be

$$q = a \cos(\omega t - \theta),$$

where the constants of integration a and θ determine the amplitude and the phase respectively, and ω is the pulsatance of the vibration. Hence the momentum p is given by

$$p = - ma\omega \sin(\omega t - \theta),$$

or

$$p = -b \sin(\omega t - \theta),$$

where b is an abbreviation for $ma\omega$.

It is easily seen that

$$\frac{q^2}{a^2} + \frac{p^2}{b^2} = 1,$$

which gives a relation between the two **co-ordinates** p and q which determine the state of the resonator. The use of the term co-ordinates here is derived from a convenient method of representing this state geometrically. We may take q and p to represent rectangular Cartesian co-ordinates in a q-p plane which is called the **state plane** or **phase plane**. Any point in this plane corresponds to some assigned momentary condition of the resonator.

The equation

$$\frac{q^2}{a^2} + \frac{p^2}{b^2} = 1$$

is that of an ellipse of semi-axes a and $b (= ma\omega)$, and of area

$$\pi ab = \pi m a^2 \omega = A \quad \text{(say)} \quad \text{(Fig. 290)}.$$
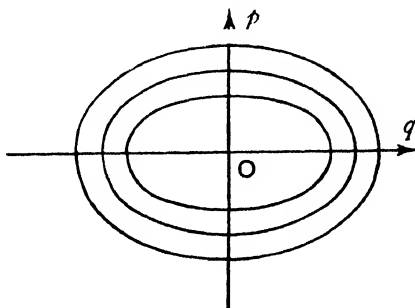
FIG. 290. PHASE DIAGRAM OF OSCILLATOR

Such an ellipse constitutes a phase-path or orbit, and the sequence of points on the ellipse *represents* the successive states of motion of the resonator.

On the classical theory the whole of the phase-plane may be densely covered with representative points, for we may choose any point whatever as an initial state and plot the phase-path through it. In Planck's first statement of the quantum theory the energy of a resonator is necessarily

an integral multiple of $h\nu$, where h is Planck's constant. This means that a discrete family of ellipses is selected from the **manifold**, that is, the complete assemblage of all possible ellipses.

The energy of a resonator is partly kinetic, E_{kin}, and partly potential, E_{pot}, where $E_{\text{kin}} = \frac{1}{2}m\dot{q}^2$ and $E_{\text{pot}} = \frac{1}{2}\mu q^2$. It is easy to show (p. 765) that the total energy, $E_{\text{kin}} + E_{\text{pot}}$, is constant throughout the motion, and that it is given by

$$\tfrac{1}{2}m\dot{q}^2 + \tfrac{1}{2}\mu q^2 = \tfrac{1}{2}\mu a^2 = \tfrac{1}{2}ma^2\omega^2 = A\nu.$$

Hence, on this theory, A, the area of the ellipse, must be an integral multiple of h. If, then, we draw on the diagram a series of similar concentric ellipses such that the area between any pair of consecutive ellipses is equal to h, the representative point must always lie on one of them.

The area of the innermost ellipse is h, that of the second $2h$, of the third $3h$, and of the nth is nh. Each ellipse corresponds to a so-called stationary state in which the resonator can remain without change of energy. But when the resonator emits or absorbs energy, the representative point jumps from one ellipse to another, the energy emitted or absorbed being an integral multiple of the energy quantum $h\nu$.

It must, however, be pointed out that Planck's result requires modification in the light of later knowledge. In Schrödinger's wave mechanics the energy of the resonator instead of being $nh\nu$ is $(n + \frac{1}{2})h\nu$. This implies that the *smallest* energy content of a resonator is $\frac{1}{2}h\nu$ and is greater than zero. This is in agreement with the hypothesis of the existence of a zero-point energy, put forward by Nernst and others.

The action of a system. In discussions of the quantum theory it is necessary to introduce an important quantity called the **action** of the system in passing from its state at some given instant to its state at a subsequent instant. This was called by Sir William Hamilton in his presentation of classical dynamics the "characteristic function".

In systems possessing only one degree of freedom the kinetic energy is

$$E_{\text{kin}} \equiv T = \tfrac{1}{2}m\dot{q}^2.$$

But the momentum $p = m\dot{q}$, so that the kinetic energy may be written as $\frac{1}{2}p\dot{q}$ or $p^2/2m$.

The **action** J of the system in passing from its position at a given instant to its position at a subsequent instant may be written

$$J = 2\int T\,dt = \int p\,dq.$$

The latter integral is to be taken along the boundary curve.

In this simple case the quantum condition as expressed by Wilson and Sommerfeld may be written

$$J = 2\oint T\,dt = \oint p\,dq = nh,$$

where the integration is to be extended over values corresponding to the period, and n is a whole number.

This result may be extended to the various co-ordinates of a dynamical system in its stationary states.

In this expression for J the quantity h (Planck's constant) appears as an *atom* of action.

Rotator.   We now consider the application of the quantum theory to the **rotator,** since this is important in connection with atomic and molecular models.   In the simplest form this system is a single particle of mass m moving uniformly in a circle of radius a about a fixed centre.

Taking ϕ as the angle between the radius vector OP (Fig. 291) and some chosen initial radius OA, we may identify the **positional co-ordinate,** q, depending on the time t, with ϕ.

The kinetic energy is $E_{\text{kin}} = \tfrac{1}{2} m a^2 \dot{q}^2$.

The potential energy is independent of ϕ since the motion is uniform, and, as a is assumed constant, we may put $E_{\text{pot}} = \text{const.}$

FIG. 291.   ROTATOR

When the kinetic energy is expressed as a function of q and $\dot{q}$, the corresponding **impulse** or **momentum co-ordinate** is determined by

$$p = \frac{\partial E_{\text{kin}}}{\partial \dot{q}},$$
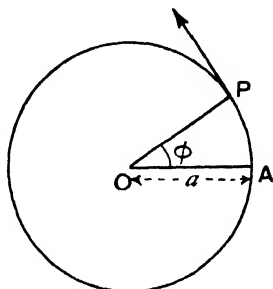
and in this case $p = m a^2 \dot{q}$, the angular momentum or the moment of momentum about the centre.   As we are assuming uniform motion for each stationary state this means that p is constant.

In the phase-plane p-q the stationary state corresponds to a straight line parallel to the q-axis.   In the rotator the conditions are repeated after every complete rotation, consequently the phase-orbit is best represented by imagining the phase-plane rolled round a cylinder of circumference 2π.   By using this artifice a plane diagram (Fig. 292) extending to infinity is replaced by the surface of a right circular cylinder.

The phase integral $J = \oint p \, dq$ taken once right round this circumference corresponds to the area $2\pi p_n$ for the nth phase-line, and for the next permitted state to $2\pi p_{n+1}$.

The general quantum condition for any system can be expressed by putting

$$J_{n+1} = J_n + h,$$

giving in this case $2\pi p_{n+1} = 2\pi p_n + h.$

It appears that for the lowest state $p_0 = 0$ according to quantum mechanics, so that $2\pi p_n = nh$, or the angular momentum $p_n = n(h/2\pi)$.

This geometrical mode of representing the states of a system is similar to that employed in statistical mechanics. The co-ordinates determining the position and velocity of a molecule are considered as fixing the position of a representative point in an imaginary space of the appropriate number of dimensions. For a point-mass having three degrees of freedom there will be needed three **positional co-ordinates,** $q(q_x, q_y, q_z)$, and three **impulse co-ordinates,** $p(p_x, p_y, p_z)$. These six co-ordinates together determine the position of a point in a space of six dimensions. For N such mass-points or molecules (considered as forming a single system), a
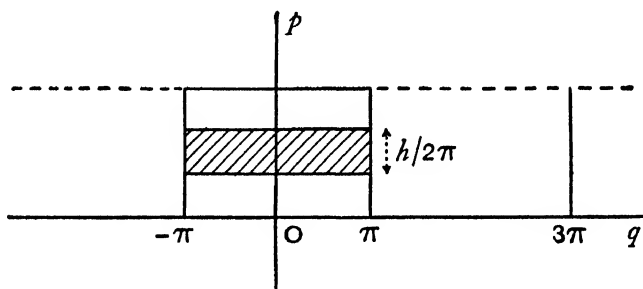
Fig. 292. Phase Diagram for Rotator

phase-space of $6N$ dimensions will be required. However, Ehrenfest has shown that the geometry of $6N$ dimensions can be converted to the geometry of 6-dimensions corresponding to each individual particle.

There is no need for alarm at the use of this geometric language, which does not imply the impossible task of " seeing " a space of six or more dimensions.

In the generalised dynamics of Sir William Hamilton the state of a physical system is determined at any instant by generalised co-ordinates typified by q and p. The values of the **positional co-ordinates** q serve to determine the position of the parts of the system, the **impulse co-ordinates** p the momenta. In the classical treatment the elementary region of probability is the extremely *small* (but still *finite*) element of the phase-space $\delta p\, \delta q \ldots$, and yet in carrying out the final calculation of probability it is customary to assume that these elements may be treated as mathematical infinitesimals, and written $dp\, dq \ldots$. Planck introduced an entirely new hypothesis which had the effect of making these elementary regions of small but definite size. The hypothesis may be stated by saying that for any pair of conjugated co-ordinates p and q

$$\iint dp\, dq = h,$$

where h is Planck's constant.

As we have seen, for *one* degree of freedom the size of the elementary region of the phase-space is equal to h. For three degrees of freedom the size of the " cell " is given by h^3.

" It was the really brilliant idea of Planck just to refuse to go to the limit. With a flash of insight he saw that in refusing to do so, and in thus denying the equipartition law, lay salvation." *

STATISTICAL TREATMENT

Statistics of an assemblage of particles. It is well known that the results derived from the consideration of an ideal monatomic gas require correction on account of the molecules of an actual gas differing from the perfectly elastic spherical molecules of the simple theory. Such corrections are exemplified in the formula of van der Waals.

But in addition to such deviations from the laws of a perfect gas there are deviations arising from the fact that quantum principles and not classical principles must strictly be employed at temperatures near the absolute zero and at high pressure, that is, in condensed states of the gas. Divergence from the classical result arising in this way is said to be due to the **degeneration** (Entartung) of the gas.

It may be pointed out here that Planck's quantum formula for the distribution of energy in the normal spectrum differs from Rayleigh's classical formula as low temperatures are approached. There is thus some resemblance between the two problems, and in each the solution has been dependent on the adoption of quantum principles.

For a detailed discussion of the statistical problem of an assemblage of particles the reader is referred to more advanced text-books.† We shall consider only some of the outstanding results of the investigation.

Let there be an assembly of N ideal gas molecules, and let us suppose that n_r molecules are assigned to the " cell " or element of hyperspace which may be represented by a_r. The ratio of n_r to the total number of molecules N is known as the **partition function.** This we denote by ω_r, so that $\omega_r = n_r/N$.

The condition of maximum probability can be obtained by employing methods similar to that used in our discussion of Maxwell's distribution law, and it is found that

$$\omega_r = \frac{1}{f} e^{-\beta \epsilon_r},$$

where f is a constant and ϵ_r is the energy of a molecule in the rth cell.

* Rice, *Introduction to Statistical Mechanics*, p. 133.

† See, for example, Rice, *Introduction to Statistical Mechanics* (Constable) ; Saha and Srivastava, *Treatise on Heat* (Allahabad) ; R. H. Fowler, *Statistical Mechanics* (Cambridge).

The symbol β is called the **modulus of distribution** and, with the aid of Boltzmann's theorem, it can be shown that $\beta = 1/kT$.

Since $\Sigma n_r = N$ we must have $\Sigma \omega_r = 1$ or $f = \Sigma e^{-\beta \epsilon_r} = \Sigma e^{-\epsilon_r/kT}$. Thus the constant f is the **sum of the partition functions** (Zustandsumme) .*

Much discussion has taken place as to the value of the constant f, because the actual value of the entropy as determined by Boltzmann's law depends upon this sum. Sackur, employing the quantum constant h and making certain assumptions, found

$$f = \frac{V}{Nh^3} (2\pi mkT)^{\frac{3}{2}}.$$

Using this value for f, the absolute value of the entropy of a perfect gas can be deduced.

Deduction of Planck's formula. The statistical results obtained for ideal gaseous molecules may be applied, with suitable modifications, to any assemblage of particles, such as atoms, electrons, or light quanta (photons), or even to vibrations in the ether. The case last mentioned is important as providing the method of Rayleigh and Jeans for deducing the radiation formula of Planck (Chapter XXXIX).

We shall now apply the condition for the state of maximum probability to the quantised paths of Planck's oscillator. The elliptic paths in the phase-space now take the place of the phase-cells in the molecular problem. In place of ϵ_r, the energy of a particle, we write $rh\nu$, which represents in the original form of the theory the energy of an oscillator in the rth quantum state.

Since the state of maximum probability is given by $\omega_r = \frac{1}{f} e^{-\beta \epsilon_r}$, we now find

$$\omega_r = \frac{1}{f} e^{-rh\nu/kT} = \frac{1}{f} e^{-rx},$$

where x is an abbreviation for $h\nu/kT$.

To determine f we make use of the condition $\Sigma \omega_r = 1$, which gives

$$f = 1 + e^{-x} + e^{-2x} + \ldots .$$

(The unity in the series arises from the lowest quantum state $r = 0$.) Hence, by means of the binomial theorem,

$$f = \frac{1}{1 - e^{-x}} .$$

The total energy of all the oscillators is the sum of the energies of the individual oscillators, that is

* In the treatise by Rice, the author uses the symbol μ in place of β, and the quantity e^λ has the value here assigned to f.

$$\text{Total energy} = \overset{r=\infty}{\underset{r=0}{\Sigma}} n_r \epsilon_r$$

$$= \overset{r=\infty}{\underset{r=0}{\Sigma}} N\omega_r \epsilon_r$$

$$= \frac{N}{f} \overset{r=\infty}{\underset{r=0}{\Sigma}} \epsilon_r e^{-rx}$$

$$= N(\mathrm{1} - e^{-x})[h\nu e^{-x} + 2h\nu e^{-2x} + 3h\nu e^{-3x} + \dots]$$

$$= N(\mathrm{1} - e^{-x})h\nu e^{-x}[\mathrm{1} + 2e^{-x} + 3e^{-2x} + \dots].$$

But we know from the binomial theorem that

$$\mathrm{1} + 2\xi + 3\xi^2 + \dots = (\mathrm{1} - \xi)^{-2}.$$

Hence,   the total energy $= \dfrac{N(\mathrm{1} - e^{-x})h\nu e^{-x}}{(\mathrm{1} - e^{-x})^2}$

$$= \frac{Nh\nu}{e^r - \mathrm{1}} = \frac{NkTx}{e^x - \mathrm{1}}.$$

Thus the *average* energy of an oscillator is

$$\frac{h\nu}{e^x - \mathrm{1}}, \quad \text{or} \quad kT \times \frac{x}{e^x - \mathrm{1}},$$

since $x = h\nu/kT$.

From this result Planck's radiation formula follows at once if we assume that the average energy of an oscillator is the same as the average energy for a mode of vibration in the " cavity radiation ". For the number of modes of vibration with frequencies between ν and $\nu + d\nu$ in a cavity of volume V as given by the Rayleigh-Jeans method * is

$$\frac{8\pi V}{c^3} \nu^2 d\nu.$$

Multiplying this number by the average energy of a mode of vibration and dividing by V, we find

$$\frac{8\pi h\nu^3}{c^3} \frac{\mathrm{1}}{e^{h\nu/kT} - \mathrm{1}} d\nu.$$

This represents the density of the energy in the frequency range $d\nu$ and is one way of expressing Planck's radiation formula.

In 1916 Einstein gave a method of obtaining the radiation formula which has interesting features but can only be mentioned briefly here. The method was based on Bohr's expression for the frequency of the monochromatic radiation emitted or absorbed in a transition between

two stationary states.   This expression, $h\nu = E_m - E_n$, is known as Bohr's
" frequency condition ".   Einstein pictured an enclosure at temperature
T, containing a large number of atoms which could exist in various
stationary states of energies E_1, E_2, ... E_r .... .   He then investigated the
condition of thermodynamic equilibrium between the atoms and the
radiation, and was able to deduce Planck's formula.

LATER STATISTICAL METHODS

Up to the present we have employed what may be called " classical "
methods of making statistical estimates, even though Planck's introduc-
tion of the quantum constant h has been permitted.   We must now turn
to certain modified methods which have been used with great success in
the interpretation of those phenomena which are subject to quantum
restrictions.   The first of these methods is due to Bose and Einstein, the
second to Fermi and Dirac.

The Bose-Einstein statistics.   " In the traditional methods of statistical
theory each particle (molecule, atom, electron) in a system is assumed
to have a recognisable individuality, and in this way one complexion
is distinguished from another, even if they are embraced in the
same state of numerical distribution of the particles between the phase
cells."

The quantum theory was introduced to overcome difficulties in the
statistical treatment of the radiation problem, and it is worth while re-
calling the fact that in obtaining Planck's radiation formula complexions
may be regarded as settled by the distribution of elements of energy
among the particles, a method leading to a modification of the mathe-
matical expression for the *a priori* probability.   In 1924 a new method
of obtaining Planck's formula was suggested by Bose, involving the
statistics of light quanta (photons) in a temperature enclosure.   The
novel feature of this paper lay in the fact that an unchanging individuality
cannot be assigned to any light quantum in the enclosure.   For the walls
are emitting and absorbing radiation, and when a quantum of frequency ν
is absorbed it may be replaced by several quanta of frequencies ν', ν'', ... ,
provided the total energy is unchanged, that is, provided ν is equal to the
sum of ν', ν'' .... .   This implies that even the number of quanta in the
enclosure is not of necessity unchangeable, there is no constancy in the
value of N.   In classical statistics it is assumed that a certain individuality
may be assigned to each particle.   But in the statistics of Bose, applied
in the first instance to light quanta, no such recognisable individuality
is ascribed to the light quantum.

To illustrate the change involved in this alteration we return to the

simple case of spinning two similar coins previously considered (p. 790). The possible events are given in the table.

Statistical states	Complexions	Weights	Probabilities
(1) Both heads - -	One	1	1/4
(2) Both tails - -	One	1	1/4
(3) One head and one tail - - -	Two	2	2/4

Here the " weight " of a given statistical state is the number of complexions corresponding to that state.

Or, regarding the problem as that of distributing two particles named a and b in two boxes, the possible arrangements are

Box 1 : $\boxed{ab}$ $\boxed{}$ $\boxed{a}$ $\boxed{b}$

Box 2 : $\boxed{}$ $\boxed{ab}$ $\boxed{b}$ $\boxed{a}$

Complexions : One   One   One   One.

When the particles are similar the number of statistical states is 3.

	Both in box 1	Both in box 2	One in each box
Complexions -	One	One	Two
Weights -	1	1	2

But in the Bose statistics, which was extended to particles by Einstein in 1925, the particles have so entirely lost all individuality that we can no longer distinguish in any way between

$\begin{cases} \text{Box 1} \ \boxed{a} \\ \text{Box 2} \ \boxed{b} \end{cases}$ and $\begin{cases} \text{Box 1} \ \boxed{b} \\ \text{Box 2} \ \boxed{a} \end{cases}$.

The arrangement with one particle in each box has then only *one* complexion instead of two. Jordan has given the following diagrammatic representation of the Bose-Einstein principle.

Box 1 : $\boxed{\cdot\cdot}$ $\boxed{}$ $\boxed{\cdot}$

Box 2 : $\boxed{}$ $\boxed{\cdot\cdot}$ $\boxed{\cdot}$

The particles having lost *all* individual distinction are represented by mere dots.

The conclusion as regards *any number* of particles in the Bose-Einstein theory is : **It is equally probable that a cell will contain any number of particles.**

Let us apply this principle to n_r particles to be distributed among a_r elementary phase-cells, disregarding individuality of the particles.

The number of ways of doing this is as shown on pages 792-3.

$$\frac{(n_r + a_r - 1)!}{n_r! (a_r - 1)!}.$$

When the number of cells is sufficiently great, this is the same as

$$\frac{(n_r + a_r)!}{n_r! a_r!}.$$

This gives for P the value

$$P = \Pi \frac{(a_r + n_r)!}{a_r! n_r!}.$$

For the equilibrium condition $\delta P = 0$, subject to the limitations as to energy $\delta E = 0$, and (for material particles) as to number $\delta N = 0$.

This leads (by using the method of undetermined multipliers) to the result

$$n_r = \frac{a_r}{f e^{\epsilon_r / kT} - 1}.$$

On the other hand, the classical theory gives

$$n_r = \frac{a_r}{f e^{\epsilon_r / kT}}.$$

The Fermi-Dirac statistics. In Bohr's theory of spectra the emission of monochromatic radiation is attributed to an electron in the outermost part of an atom making a transition from one stationary state to another. The data of spectroscopy require the introduction of *four* quantum numbers to specify the state of this " optical electron ". In 1925 Pauli of Hamburg extended this result as to four quantum numbers being required for this particular electron to all the electrons of the atom. Every electron orbit is now defined by means of four such numbers, and a given set of these four numbers defines one single orbit. Pauli's **exclusion principle** (" Verbot ") affirms that in any given orbit there can be one electron and one electron only ; or, in other words, no two electrons can exist in the same quantum state.

It is interesting to observe in passing that one of these four quantum numbers (usually designated s) is used to describe a kind of polarisation of the electron, which may be regarded as a " spin " of the electron about an axis. This implies that in addition to its electrostatic properties the electron may be pictured as a little magnet having its axis coinciding with the axis of spin. A proton likewise is to be regarded as associated with spin about an axis—with the result that hydrogen gas must be treated as a mixture of two kinds of hydrogen (ortho- and para-hydrogen). The

difference between these hydrogen molecules may be illustrated very roughly by picturing the proton-magnets as pointing in the same direction in one set of molecules and in opposite directions in the other set. This, however, is only a crude representation and the real distinction is of a more subtle character.*

The remarkable principle enunciated by Pauli has proved of the greatest value in the study of atomic structure. By means of it we can determine the distribution of electrons in successive atomic levels, and are led to an interpretation of the periodic classification of the elements. Further, it has been extended by Heitler and London (1927) to molecules, and is of importance in dealing with molecular structure. The new quantum mechanics provided some measure of theoretical justification for Pauli's principle as applied to electrons in atoms. Heisenberg and Dirac have shown independently that the principle possesses a natural basis on these theories.

In 1926 Fermi and independently Dirac suggested that in dealing with the statistics of systems of particles an analogous exclusion principle should be employed. For this purpose the principle may be stated in the form : two or more representative points can never occupy one and the same energy cell; in other words, we are restricted to putting in a single cell either one representative point or none.

Employing the previous illustration of two particles and two cells, the only possible arrangement is that with *one* particle in each cell.

$$\boxed{\;\cdot\;}$$
$$\boxed{\;\cdot\;}$$

When the intrinsic probability is once settled, the steady state corresponding to maximum probability can be found by the usual methods.

Application to an ideal gas.   The statistical method of Fermi and Dirac may be applied to an assemblage of molecules forming an ideal gas. In this case we disregard rotation of the molecules and ascribe *three* quantum numbers (n_1, n_2, n_3) to each molecule, these numbers corresponding to the three degrees of translation. The number of complexions in which the energy $nh\nu$ (say) can be realised is the number of solutions of the indeterminate equation, $n_1 + n_2 + n_3 = n$. The number of such solutions is $\frac{1}{2}(n+1)(n+2)$. For example, there can be only one molecule with zero energy, only three molecules with energy $h\nu$, only six with energy $2h\nu$, only ten with energy $3h\nu$, and so on. Here ν is a fundamental frequency characteristic of the gas, and for a gas contained in a vessel this is determined by the size of the vessel.

* C. G. Darwin, *The New Conceptions of Matter*, Chapter VIII Bell, 1931).

The application of these principles leads to the conclusion that even at the absolute zero of temperature neither the energy nor the pressure of the gas can vanish.

The departure from the classical laws is known as the **degeneration** of the gas (p. 825) and the degree of degeneration depends on the product mT, the mass of a gaseous molecule and the absolute temperature. The smaller the value of this product the greater is the degree of degeneracy. The smaller the mass m the higher is the value of T at which a state of degeneration can be realised. When allowance is made for spin the theory can be extended to an "electron gas", and since in this case m is very small, there is complete degeneration even at room temperature.

The results obtained by applying the Fermi-Dirac statistics to material particles depend on the value of the quantity f (defined on p. 826). For an ordinary gas having n molecules in each unit of volume we take

$$f = \frac{(2\pi mkT)^{\frac{3}{2}}}{nh^3},$$

while for an electron gas this value must be multiplied by the factor 2 because of the existence of "spin".

The criterion for determining degeneracy depends on the value of f. When f is large compared with unity there is *no* degeneracy and the Maxwellian results hold good; when, on the other hand, f is small compared with unity, degeneracy is present and the degree of degeneracy increases as f diminishes. Formulae have been obtained * in the region of weak and of strong degeneracy for the pressure of a gas from which it appears that with helium at $5°$ K. and 7 atmospheres (weak degeneracy) the deviation from the classical result is about 10 per cent. At very low temperatures ($T \rightarrow o$) the pressure approaches a limiting value. The mean kinetic energy of a molecule also approaches a limiting value as $T \rightarrow o$. The specific heat of a gas at constant volume is given by

$$C_v = \sqrt[3]{\frac{16\pi^8}{9} \frac{mk^2T}{h^2n^{\frac{2}{3}}}}$$

and is thus proportional to the absolute temperature.

Special interest attaches to the expression for the entropy S, which is found to be

$$S = nk\left[\tfrac{3}{2}\log_e T - \log_e n + \log_e \frac{(2\pi mk)^{\frac{3}{2}}e^{\frac{5}{3}}}{h^3}\right],$$

where e is the base of the natural logarithms here employed.

* See, for example, Castelfranchi, *Recent Advances in Atomic Physics*, pp. 357-369, where the reciprocal of f is called A.

•This result agrees exactly with that given by Tetrode, Stern and Sackur (p. 826). The expression for the entropy can also be written in the form

$$S = Nk \log_e \left[\frac{V}{N h^3} (2\pi mkT)^{\frac{3}{2}} e^{\frac{5}{2}} \right],$$

where N is the number of molecules in volume V.

Comparison of the different statistics. * It is interesting to compare with one another the results obtained by applying the different statistical methods we have considered to the distribution of energy amongst the molecules of a gas (or other material particles).

We take n_s to denote the number of these particles having their energy between the limits ϵ_s and $\epsilon_s + d\epsilon_s$.

We find, on the classical theory,

$$n_s = \frac{a_s}{f e^{\epsilon_s/kT}}.$$

According to the Bose-Einstein statistics,

$$n_s = \frac{a_s}{f e^{\epsilon_s/kT} - 1};$$

and according to the Fermi-Dirac statistics,

$$n_s = \frac{a_s}{f e^{\epsilon_s/kT} + 1}.$$

It will be seen that all three results may be included in the formula

$$n_s = \frac{a_s}{f e^{\epsilon_s/kT} + c},$$

where c is a constant which may assume the value o, or ± 1.

The fact that three formulae at first sight so similar should lead, under suitable conditions, to very different results depends, of course, on the relative magnitude of the two terms which appear in the denominator. On the other hand, it may seem strange that satisfactory results have been obtained by using classical statistics when the principles of selection in the newer statistics are so strikingly different. The reason for this has been given by Fowler. It lies in the extremely small value of the quantum constant h. In consequence of the small value of h the phase-space has so many cells of extension h^3 that it is extremely improbable that any pair of representative points will attempt to occupy the same cell. Darwin and Fowler consider a gram-molecule of gas under standard conditions with a volume of about 20 litres. There will be about 10^{63} elementary cells in the whole extension, but only about 10^{24} representative points to partition among them!

* For further details reference may be made to the *Treatise on Heat* by Saha and Srivastava.

They also draw attention to the weak point in using Stirling's theorem in such a case, for the use of this theorem implies that the points available are far more numerous than the cells. They therefore propose a new treatment of the problem, involving the method of " contour integration ", in which the *average* state of a system is considered rather than the *most probable* state.

UNDULATORY MECHANICS

Wave mechanics. Quantum mechanics affords a remarkable illustration of the power of mathematical methods and especially of the fact that very different modes of treatment lead to essentially the same conclusions. To the physicist the wave mechanics of Schrödinger made a strong appeal because it gave promise of providing a pictorial representation and not merely a collection of symbols. This hope was in large measure disappointed when it was realised that the complex function ψ (psi) which satisfied the wave equation must be regarded as a probability. The conception of de Broglie (1923) that the electron may be considered as a " wave packet " or a singularity in a wave phenomenon has been replaced by the statistical view on which the wave becomes a purely symbolic and analytic representation of certain probabilities. The ψ-function itself is only a mathematical auxiliary quantity, and it is its " norm " (the product of ψ and the conjugate complex quantity), which, when multiplied by e, the electron charge, has a physical meaning, namely the average value of the charge-density at some particular position. The older picture of individual electron orbits now becomes less distinct, and we may regard the charge-density as representing the average time of stay of the electron in each individual position.

M. de Broglie has summarised the conception of wave mechanics as follows : " The fundamental postulate of the wave mechanics is that with every independent particle, whether of matter or of radiation, there is associated the propagation of a wave, the *intensity* of this wave representing at each point and at each instant the *probability* that the associated particle will reveal itself at this point at this instant."

R. H. Fowler has examined a very general form of statistical mechanics which includes as special cases the classical form, that of Bose-Einstein and that of Fermi-Dirac. He assumes that the possible states of any *system* in the assembly are defined by the energy values, and these must be the characteristic values of Schrödinger's equation for that system. He finds that the Einstein-Bose statistics is required for those systems whose wave functions are of the **symmetrical** group, the Fermi-Dirac statistics is required for those systems whose wave functions are of the **anti-symmetrical** group.

The terms " symmetric " and " antisymmetric " require some explana-

tion. A suggestive analogy is afforded by the terms " parallel " and " antiparallel ". When two similar magnets are placed side by side (Fig. 293) with their axes parallel, *two* positions are possible : the north

Parallel   **Anti-parallel**
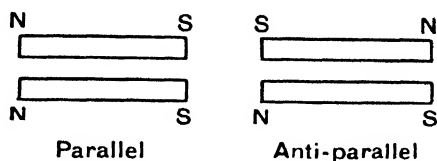
FIG. 293. PARALLEL AND ANTIPARALLEL SYSTEMS OF MAGNETS

pole of one may be opposite the south pole of the other, in which case the magnets attract one another ; or the two north poles may be opposed, and likewise the two south poles, in which case the magnets repel one another. If the magnets are of sufficient strength (say of cobalt-chrom steel) the repulsion may be great enough to support the entire weight of the second magnet. This is the case in the well-known experiment in which a magnet is held suspended in air, like Mahomet's coffin, because of the repulsion due to a second magnet. It should be observed that in this experiment means must be provided to prevent rotation of the suspended magnet, otherwise the magnet will tend to turn so that its axis instead of being in the parallel is in the antiparallel position.

Now consider two similar dynamical systems, each of which is capable of executing oscillations of some definite period. Two spiral springs each carrying a given load may serve as an illustration. If the upper ends of the springs are attached to a horizontal lath of wood supported at its two ends, we have an arrangement that may be called a " coupled system ". There are two characteristic modes in which the system may vibrate. It may happen that both loads move downwards at the same time, and also move upwards at the same time. This we call the symmetric mode of oscillation. But again it may happen that while one load is moving downwards the other is moving upwards, the movements keeping in step with one another. This is what we call the antisymmetric mode of oscillation. It is not that there is an entire absence of symmetry, in that case we should use the term " asymmetry " ; but there is a kind of perverted symmetry.

Symmetrical and antisymmetrical wave functions. In discussing, on the basis of quantum mechanics, systems containing several similar particles, one of the most important distinctions to be drawn is that between symmetrical and antisymmetrical wave functions (*Eigenfunctionen*). We say that the wave function is symmetrical in a number of systems if the function does not alter when any pair of the numbers specifying the systems is interchanged. On the other hand, the wave

function is antisymmetrical in the systems if the function changes sign when any pair of these numbers is interchanged. If a wave function is initially symmetrical, it always remains symmetrical ; if a wave function is initially antisymmetrical it always remains antisymmetrical. The symmetry properties of the states are both invariant and permanent.

The wave function representing the whole atom can be built up from wave functions representing the different electronic orbits. Provided the wave functions for the electrons are antisymmetric, the combination of wave functions applicable to the whole group necessarily vanishes. " Hence if we assume that for electrons only antisymmetrical states occur, we shall get the result that there are no two electrons in the same orbit. This assumption is the only one we can make which will lead to Pauli's exclusion principle " (Dirac). This choice of antisymmetric wave functions corresponds to the use of Fermi-Dirac statistics.

According to the view adopted both by Heisenberg and Dirac, Pauli's exclusion principle possesses a natural basis in the new statistics. On the basis of this principle it is possible to forecast the arrangement of the elements in the periodic table. Fowler concludes that the number of electrons to be found in groups and subgroups of the elements in the table " may now be regarded as a formal deduction from the new atomic mechanics ".

Dirac * further points out that for any particular type of particle we can only settle the question of the kind of wave function to be employed by appeal to experimental facts. Suppose, for instance, the particles are photons or light quanta. Experimental results indicate that Planck's radiation formula applies in the equilibrium state. It is only when we assume that photons are represented by symmetric wave functions that we arrive at a statistical mechanics leading to the law. This means that the Einstein-Bose statistics is to be used for photons.

Suppose we have an assembly of atomic systems which can be treated properly as practically independent. We may then consider the wave functions for groups of similar atoms, molecules or ions, which represent their motions as wholes, not their internal structure. We find that " the wave-functions must be *antisymmetrical* if the system contains an *odd* number of electrons and protons and *symmetrical* if it contains an *even* number ". Applying this rule to an ordinary gas which has not been electrified or ionised, we see that " the wave-functions for gaseous assemblies of practically independent *neutral* atoms or molecules must be *symmetrical* for each set of similar atoms or molecules ".

When the systems are electrons or protons it is certain that wave functions of the antisymmetrical group must be employed. For electrons

* *The Principles of Quantum Mechanics*, p. 212 (1935).

this follows from the fact that the laws of interaction of electrons must embody Pauli's exclusion principle. The antisymmetrical group is the only group of wave functions of the assembly which possesses just this property, that it has no member whenever two systems have the same wave function.

Light quanta or photons, in contradistinction to electrons, must be assumed to behave in such a way that their wave functions always belong to the symmetrical group.

It is well known that correct results can be obtained for radiation in an enclosure by regarding the radiation as a set of standing waves in a single system, "the aether". This was the method employed by Rayleigh and Jeans. In the alternative picture, "radiation is regarded as made up of numbers of independent systems, some of which may be identical, and the correct method of counting complexions at once becomes of primary importance. The essence of the theory of Bose and Einstein is that they prove that the light-quantum picture does give a complete self-consistent result, with a consistent mechanism of interaction, if we regard the light quanta as quasi-particles and count complexions " in the appropriate way.

For an electron gas, such as that considered by Sommerfeld in dealing with electric conduction in metals, we must employ the Fermi-Dirac statistics. Even at ordinary temperatures the electron gas must be in a state of almost complete degradation. This is because the mass of an electron is very small in comparison with the mass of even the lightest atom. The result has most important consequences in the theory of heat, because it follows that the contribution made by the electrons to the specific heat of the metals is insignificant. For a long period no satisfactory explanation could be given of the fact that observed specific heat could be accounted for by the atoms alone. By Sommerfeld's theory, in which the electrons in a metal are treated from the standpoint of the new statistics, "the great stumbling-block of the negligible contribution of the electrons is surmounted at the first stride ". The theory also gives a satisfactory account of thermal conductivity and of thermo-electric phenomena.

We may conclude this survey in the words of Max Born : " The new quantum mechanics assumes that all laws of physics are of statistical character. The fundamental quantity is a wave function which obeys laws similar to those of an acoustical or optical wave ; it is not, however, an observable quantity, but determines indirectly the probability of observable processes ".

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QUESTIONS

CHAPTER XLIV

1. Derive an expression for a resonator executing simple harmonic motion, and show that on the Quantum Theory the area of the defining ellipse must be an integral multiple of Planck's Constant.

2. What do you understand by *the action of a system*? Apply your definition to the case of a single particle of mass m moving uniformly in a circle of radius a about a fixed centre. How is this conception modified under quantum conditions?

3. Write an account of the degeneration of a gas.

4. In what way do the statistical methods of Bose and Einstein and of Fermi and Dirac differ from Planck's " classical " methods of making statistical estimates?

5. Give a short description of the method in which " wave mechanics " has been applied to atomic theory.

MISCELLANEOUS QUESTIONS

PART II

1. Calculate the rate of heat production when a wire of 10 ohms resistance is traversed (*a*) by a direct current of 10 amperes, (*b*) by an alternating current whose maximum value is 10 amperes. (E U. M.A.)

2. Find an expression for the velocity with which a wave of compression travels through a gas. Discuss the way in which the expression for the velocity is affected by the theoretical assumptions made as to the thermal condition of the gas during the passage of the wave.

3. Give an account of the scientific work of *one* of the following : Newton, Joule, Faraday. (O. & C H S C.)

4. State Newton's law of cooling, and show that the temperature of a body which cools according to this law is given by $v -v_0 e^{-ct}$ where v denotes the difference in temperature of the body and its surroundings.

The temperature of a vessel filled with hot water and left to cool by radiation in a room at temperature $13 \cdot 0^\circ$ C. was $44 \cdot 6^\circ$, $26 \cdot 8^\circ$, $19 \cdot 7^\circ$, $15 \cdot 2^\circ$, and $14 \cdot 2^\circ$ C. after 0, 36, 71, 126, and 154 minutes respectively. Graph $\log v$ as a function of t, and so determine the numerical value of c.

5. Write a short account of (*a*) the thermal conductivity of a gas ; (*b*) the Joule-Thomson effect. (E.U. Inter. Hons.)

6. Write *brief* accounts of *two* of the following :

(*a*) The solar constant ;
(*b*) The effective temperature of the sun ;
(*c*) Convective equilibrium in the atmosphere. (E.U. M.A. Hons.)

7. Explain the red colour of (1) a coke fire, (2) a dark-room lamp, (3) a strontium flame, (4) a piece of copper, and (5) the setting sun. (E.U M.A.)

8. Discuss from the point of view of the molecular theory of gases the question of internal energy and specific heat. (E.U. Inter. Hons.)

9. Discuss the significance of the equation of state of van der Waals, with special reference to the constants involved, and find the values of the critical pressure, volume, and temperature in terms of these constants. (St. A. U.)

10. Write an account of the equation of van der Waals, and show how to obtain relations between the critical constants of a substance and the constants of this equation. (E.U. M.A.)

11. What are the reasons which have led to the introduction of the constants a and b into the van der Waals's equation for a gas, and what physical meanings do you attach to the constants ? How can they be connected with the critical point of the gas ? (L.U. B.Sc.)

12. Explain, without theoretical proofs, the way in which the following quantities are represented on a thermoelectric diagram :
Peltier coefficient, Thomson coefficient, the total E.M.F. in a thermoelectric circuit, and the amounts of heat absorbed reversibly in such a circuit.
Give an account of a method of measuring the rate of heat emission from a radioactive substance, employing a thermoelectric circuit. (E.U. M.A. Hons.)

13. Write a short account of the kinetic theory of gases as applied in obtaining the simple gas equation, indicating how the simple gas equation has to be modified when the molecules are no longer regarded as mass-points. (St. A. U.)

14. State briefly the chief assumptions made in the elementary kinetic theory of gases, and explain how far these were corrected by van der Waals. What is meant by the root mean square velocity of the molecules of a gas? Calculate its numerical value in the case of hydrogen at $0°$ C., given that the density of hydrogen at N.T.P. is 0.00009 gm./c.c. (L.U. B.Sc.)

15. What do you understand by the term " triple point "? Discuss its properties, taking water as an example, and paying special attention to the slopes of the steam-ice and hoar-frost lines. (L.U. Spec. B.Sc.)

16. State the principle of equipartition of kinetic energy, and from this deduce an expression for the ratio of the specific heats of a polyatomic gas. What is the theoretical value of this ratio (a) for a monatomic gas, (b) for a diatomic gas? How do these values agree with the experimental results? (St. A. U.)

17. Give a general account of Debye's theory of the specific heat of a solid. (St. A. U.)

18. Write an account of the specific heats of solids with special reference to their temperature relations.
Give an outline of the way in which the quantum theory has been employed to explain the observations. (St. A. U.)

19. Discuss the determination of the specific heat of hydrogen at temperatures from atmospheric downwards, and the importance of the results for molecular theory. (L.U. Spec. B.Sc.)

20. Assuming that the molecular energy of a gas is equally distributed among the degrees of freedom of the molecules, show that the ratio of the specific heats is equal to $1 + 2/n$, where n is the number of degrees of freedom per molecule. Discuss the information about the internal structure of molecules which can be obtained from this result. (St. A. U.)

21. Discuss the method of obtaining information regarding the structure of a molecule of a gas by determining its specific heats, volume constant and pressure constant, and their variation with temperature. (St. A. U.)

APPENDIX I
FUNDAMENTAL PHYSICAL CONSTANTS

Velocity of light	c	$= 2\cdot99776$	$\times 10^{10}$ cm. sec.$^{-1}$.
Electron charge	e	$= 4\cdot8025$	$\times 10^{-10}$ e.s.u.
Specific electron charge	e/m	$= 1\cdot7592$	$\times 10^{7}$ e.m.u. gm.$^{-1}$.
Planck's constant	h	$= 6\cdot624$	$\times 10^{-27}$ erg. sec.
Faraday's constant *	F	$= 9\cdot6514$	$\times 10^{3}$ e.m.u. (gm. equiv.)
Avogadro's constant †	N	$= 6\cdot0228$	$\times 10^{23}$ mole^{-1}.
Mass of molecule of mol. wt.	M	$= M(1\cdot66035 \times 10^{-24})$ gm.	
Atomic weight of hydrogen	^1H	$= 1\cdot00813$.	
Mass of hydrogen atom	M_H	$= 1\cdot67339$	$\times 10^{-24}$ gm.
Mass of the electron	m	$= 9\cdot1066$	$\times 10^{-28}$ gm.
Mass of the proton	M_P	$= 1\cdot67248$	$\times 10^{-24}$ gm.
Gas constant for 1 mole	R_M	$= 8\cdot31436$	$\times 10^{7}$ erg. deg.$^{-1}$ mole^{-1}.
Boltzmann's constant	k	$= 1\cdot38047$	$\times 10^{-16}$ erg. deg.$^{-1}$.
Volume of one mole at N.T.P.		$= 22\cdot414$ litres.	
Fine structure constant	α	$= 2\pi e^2/hc = 7\cdot2976_6 \times 10^{-3}$.	
Reciprocal of α	$1/\alpha$	$= 137\cdot030$.	
Rydberg's constant	R_∞	$= 109737\cdot303$ cm.$^{-1}$.	
One electron volt		$= 1\cdot60203 \times 10^{-12}$ erg.	
Joule's equivalent	J	$= 4\cdot1855$ joule cal.$^{-1}$.	
Ice point	T_0	$= 273\cdot16°$ K.	

Based on the results recorded for the General Physical Constants as of August 1941 by Raymond T. Birge (*Reports on Progress in Physics*, vol. viii, p. 90, 1941, The Physical Society, London). These values form a *consistent* system. The values of the constants given above differ slightly from those in the *International Critical Tables* (1926) and from those given by Birge in the *Physical Review Supplement* (1929). The earlier results of Birge are frequently quoted in the text, but as a consequence of much critical work " the situation in respect to the general constants is now vastly improved over that obtaining in 1929 ".

* This is the value of the Faraday constant on the *physical* scale, based on the assumption that the ordinary isotope $^{16}O = 16\cdot0000$. Two other isotopes of oxygen are known (^{17}O and ^{18}O) and the *chemical* scale is based on the assumption that atomic weight of the mixture is $16\cdot0000$. On the latter scale the Faraday constant has the value $9\cdot6487 \times 10^3$.

† This is the value of Avogadro's constant on the *chemical* scale.

APPENDIX II

PHYSICAL CONSTANTS OF THE ELEMENTS

THE following table contains some of the more important physical constants of the chemical elements. The columns are numbered from left to right, and give the following information where available :

1. The atomic number, Z.

2. The name of the element.

3. The accepted chemical symbol.

4. The atomic weight, assuming $O = 16 \cdot 000$, accepted in the year 1938.

5. The density in gm. cm.$^{-3}$ for the solid state, or in some instances (marked l) for the liquid state.

6. The melting point *on the absolute scale* (°K.).

7. The boiling point (approximate) at a pressure of 760 mm. *on the absolute scale* (°K.).

8. The specific heat, in most cases at room temperature (indicated by R). In some cases the range of temperature (approximate) is indicated. The letter I is used for the ice-point and S for the steam-point. The specific heat is in cal. gm.$^{-1}$ °C.$^{-1}$.

9. The latent heat of fusion in cal. gm.$^{-1}$. Many of these results are somewhat uncertain.

For coefficients of expansion see page 87, and for coefficients of thermal conductivity see page 390.

PHYSICAL CONSTANTS OF THE ELEMENTS

1 Z	2 Element	3 Symbol	4 A	5 ρ	6 M.P °K.	7 B.P. °K.	8 S.H.	9 L.H.
1	Hydrogen	H	1·0081	—	—	—	—	—
2	Helium	He	4·003	0·23	—	—	—	—
3	Lithium	Li	6·940	0·534	459	>1670	I-S 1·093	—
4	Beryllium	Be	9·02	1·83	1554	1770 sublimes	I-S 0·425	—
5	Boron	B	10·82	2·5	c. 2500	3770	I-S 0·307	—
6	Carbon {Diamond {Graphite	C	12·010	D. 3·52 / G 2·3	c. 3770	4470	R 0·16	—
7	Nitrogen	N	14·008	l 0·79 (77° K.)	62·7	77·5	0·028	—
8	Oxygen	O	16·000	s 1·32 / l 1·27 (38° K.) / l 1·11 (86° K.)	54	90·3	0·35	—
9	Fluorine	F	19·00	l ?	50	86	—	—
10	Neon	Ne	20·183		24·5	27·3	—	—
11	Sodium	Na	22·997	0·971	370·8	1150	I 0·283	27·5
12	Magnesium	Mg	24·32	1·74	932	1390	R-S 0·247	46·5
13	Aluminium	Al	26·97	2·70	930	2070	R-S 0·217	92·4
14	Silicon	Si	28·06	$2\cdot32_7$	1688	3770?	R 0·17	—
15	Phosphorus	P	31·02	red 2·20 / yel. 1·83 / rh. 2·07	317	660	R-S 0·17 / R 0·202	5
16	Sulphur	S	32·06	mon 1·96	388 392	717·8	R 0·163	9
17	Chlorine	Cl	35·457	l 2·49	171	238·6	R 0·226	—
18	Argon	A	39·944	l 1·4 (88° K.)	85	87	—	16
19	Potassium	K	39·096	0·862	335·7	1031	R 0·19	—
20	Calcium	Ca	40·08	1·55	1124	1440	R 0·149	—
21	Scandium	Sc	45·10	—	—	—	—	—

PHYSICAL CONSTANTS OF THE ELEMENTS—*Continued*

1 Z	2 Element	3 Symbol	4 A	5 ρ	6 M.P. °K.	7 B.P. °K.	8 S.H.	9 L.H.
22	Titanium -	Ti	47·90	4·5	2073	—	R 0·142	—
23	Vanadium -	V	50·95	6·0	1993	—	I-S 0·115	—
24	Chromium -	Cr	52·01	7·1	2103	2470	I 0·104	32
25	Manganese	Mn	54·93	7·39	1515	2170	I-S 0·110	—
26	Iron	Fe	55·84	7·87	1803?	2720	I 0·1045	49
27	Cobalt -	Co	58·94	8·6	1753	3170	R-S 0·104	58
28	Nickel -	Ni	58·69	8·9	1725	2600?	R-S 0·109	65
29	Copper -	Cu	63·57	8·93	1356	2580	R-S 0·093	43
30	Zinc -	Zn	65·38	7·1	691	1191	I 0·092	26·6
31	Gallium -	Ga	69·72	5·95	303·4	—	R 0·079	—
32	Germanium -	Ge	72·60	5·47	1233	sublimes	I-S 0·074	—
33	Arsenic -	As	74·91	am. 5·73 / cr. 4·8	—	720	I-S 0·08	—
34	Selenium -	Se	78·96	4·5	490	960	0·095 / 0·084	—
35	Bromine -	Br	79·916	*l* 3·102	265·9	332	s 0·084 / l R 0·107	16
36	Krypton -	Kr	83·7	2·16	104	121·5	—	—
37	Rubidium -	Rb	85·48	*l* 1·532	311·7	969	0·08	—
38	Strontium -	Sr	87·63	2·54	1044	1423	—	—
39	Yttrium -	Y	88·92	3·8?	—	—	—	—
40	Zirconium -	Zr	91·22	6·5	c. 1970	—	I-S 0·067	—
41	Niobium * -	Nb	92·91	8·5	1223	—	—	—
42	Molybdenum -	Mo	95·95	10·0	2720?	3470?	R-S 0·072	—

* or Columbium Cb.

PHYSICAL CONSTANTS OF THE ELEMENTS—Continued

1 Z	2 Element	3 Symbol	4 Å	5	6 M.P. °K.	7 B.P. °K.	8 S.H.	9 L.H.
43	Ruthenium -	Ru	101·7	12·3	2170?	2790?	I-S 0·061	—
44	Rhodium -	Rh	102·91	12·44	c. 2240	2470?	R-S 0·058	—
45	Palladium -	Pd	106·7	11·4	1822?	2810	R-S 0·059	36
46	Silver -	Ag	107·880	10·5	1233·7	2228	R-S 0·056	22
47	Cadmium -	Cd	112·41	8·64	594	1051	R 0·055	14
48	Indium -	In	114·76	7·3	428	1270?	I-S 0·057	—
49	Tin -	Sn	118·70	7·29	505	2540	R 0·054	14·6
50	Antimony	Sb	121·76	6·68	903	1710	R 0·050	24·3
51	Tellurium -	Te	127·61	6·25	723	1660	R-S 0·048	—
52	Iodine -	I	126·92	4·95	386	457·6	R-S 0·054	12
53	Xenon -	Xe	131·3	3·5	133	164	—	—
54	Caesium -	Cs	132·91	1·87	299·6	943	R 0·048	—
55	Barium -	Ba	137·36	3·75	977	1410	R 0·07	—
56	Lanthanum -	La	138·92	6·12	1099	—	I-S 0·045	—
57	Cerium -	Ce	140·13	6·92	896	1670	I-S 0·045	—
58	Praseodymium -	Pr	140·92	6·48	1213	—	—	—
59	Neodymium -	Nd	144·27	5·96	1113	—	—	—
60								
61								
62	Samarium -	Sm	150·43	7·8	1623	—	—	—
63	Europium -	Eu	152·0	—	—	—	—	—
64	Gadolinium -	Gd	156·9	5·91	—	—	—	—
65	Terbium -	Tb	159·2	—	—	—	—	—
66	Dysprosium -	Dy	162·46	—	—	—	—	—
67	Holmium -	Ho	163·5	—	—	—	—	—
68	Erbium -	Er	167·2	4·77?	—	—	—	—

PHYSICAL CONSTANTS OF THE ELEMENTS—*Continued*

1 Z	2 Element	3 Symbol	4 A	5 ρ	6 M.P. °K.	7 B.P. °K.	8 S.H.	9 L.H.
69	Thulium	Tm	169·4	—	—	—	—	—
70	Ytterbium	Yb	173·04	5·5	—	—	—	—
71	Lutecium	Lu	175·0	—	—	—	—	—
72	Hafnium	Hf	178·6	—	—	—	—	—
73	Tantalum	Ta	180·88	16·6	3073?	—	58° C. 0·036	—
74	Tungsten	W	183·92	19·3	3633?	3970?	R-S 0·034	—
75	Rhenium	Re	186·31	—	—	—	—	—
76	Osmium	Os	190·2	22·5	2973	—	R-S 0·031	—
77	Iridium	Ir	193·1	22·41	c. 2720	—	R-S 0·0323	—
78	Platinum	Pt	195·23	21·50	2046?	4570?	R-S 0·0322	27
79	Gold	Au	197·2	19·32	1335	2800	R-S 0·031	16
80	Mercury	Hg	200·61	l 13·56 / s 14·19	234·36	629·9	R 0·033	3
81	Thallium	Tl	204·39	11·9	574	1550	R-S 0·033	—
82	Lead	Pb	207·21	11·37	600	1890	R-S 0·0305	5
83	Bismuth	Bi	209·00	9·80	542	1690	R-S 0·0303	13·0
84	Polonium	Po	210	—	—	—	—	—
85								
86	Radon	Rn	222	—	—	—	—	—
87								
88	Radium	Ra	226·05	—	1233	—	—	—
89	Actinium	Ac	226·7	—	—	—	—	—
90	Thorium	Th	232·12	11·3	1963	—	I-S 0·028	—
91	Ux₂	Ux₂	234	—	—	—	—	—
92	Uranium	U	238·07	18·7	2133	—	I-S 0·03	—

PART II

SYMBOLS FOR PHYSICAL QUANTITIES

This list is intended to supplement that given in Part I on page 526. The meanings of some of the more important symbols are, however, repeated here.

A	work ; activity
C	specific heat
c	velocity of light
d	perfect differential
E	energy ; surface emissivity
F	Helmholtz free energy
F_0	the faraday
f	sum of the partition functions
G	Gibbs free energy
H	enthalpy or total heat ; heat of reaction
h	rate of transfer of heat or thermal transmission
h	Planck's constant
J	Joule's equivalent ; action
K	thermal conductivity
k	diffusivity of temperature ; Boltzmann's constant
L	latent heat
P	possibility number
p	impulse co-ordinate
Q	quantity of heat
q	positional co-ordinate
R	gas constant
S	entropy
s	molecular diameter
T	temperature on gas scale
T_0	ice point
U	intrinsic or internal energy
W	probability
w	mean molecular energy
z	electrochemical equivalent

GREEK SYMBOLS

β modulus of distribution

γ ratio of specific heats

Δ coefficient of diffusion ; increment

ϵ efficiency ; element of energy

η coefficient of viscosity

θ temperature in general

κ undulatance

λ mean free path

ν frequency ; kinematical viscosity

Π product

Σ sum

σ surface tension ; Stefan's constant

τ temperature on thermodynamic scale

ω pulsatance

ω_r partition function

MISCELLANEOUS SYMBOLS

$\oint$ cyclic integral

∇ nabla or del, a vector operator

!   factorial, thus $n! = n(n-1)(n-2) \ldots 3 . 2 . 1$

ANSWERS TO QUESTIONS

CHAPTER XXVII

1. -54.7 °C.

2. 1.87×10^9 ergs.

3. 2.70×10^9 ergs.

4. 0.370×10^{10} ergs.

5. 0.1554 cal. gm.$^{-1}$ °C.$^{-1}$; 1.40.

6. 0.0021 cal. gm.$^{-1}$ °C.$^{-1}$.

CHAPTER XXIX

8. 1.10×10^{11} ergs.

9. 4.12×10^3 cal.

CHAPTER XXX

4. 8.79 cal. °C.$^{-1}$.

5. 3.99 cal °C.$^{-1}$.

6. 2.12 cal. °C.$^{-1}$.

7. 0.0585 cal. °C.$^{-1}$

8. (*a*) 21.13 cal. °C.$^{-1}$; (*b*) 20.81 cal °C.$^{-1}$; (*c*) 21.55 cal. °C.$^{-1}$; (*d*) 20.17 cal. °C.$^{-1}$; (*e*) 20.15 cal °C.$^{-1}$.

9. 8.40 cal °C.$^{-1}$.

CHAPTER XXXI

2. 2.39 cal. °C.$^{-1}$; 0.0052 °C   **3.** 322 c.c. gm.$^{-1}$.   **6.** 1.033 cal. gm.$^{-1}$ °C.$^{-1}$.

7. 358.7 c.c gm.$^{-1}$.   **10.** 27.34 mm. of Hg.   **12.** -0.0074 °C.

13. 1658 c.c.   **14.** 0.036 °C.   **16.** $v_2 - v_1 = c\theta + a\theta^{-1}$.   **18.** 162 c.c.gm.$^{-1}$.

CHAPTER XXXIV

4. 273.16 °K.   [We may calculate an approximate value for the ice-point from the data supplied by assuming that the differential coefficient on page 689 is the same as for the air-thermometer, treating air as a perfect gas.]

CHAPTER XXXV

4. 7.05 cal./sec.

6. 283 cm.

CHAPTER XXXVII

4. 73.1 cal./sec.

5. 1.55×10^{-9} dyne cm^{-2}

CHAPTER XXXVIII

6. $7.48 : 1$.

INDEX

The letter *f.* following a page number denotes that the reference is to a footnote only

2X3

II